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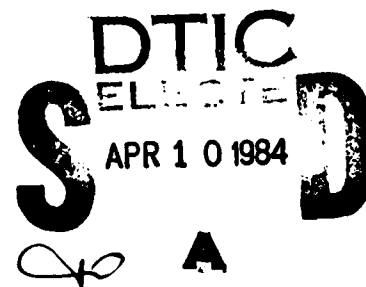
Hydrocarbons Utilizing Elemental Fluorine

by

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This document concludes the Office of Naval Research sponsored development of the Aerosol Fluorination Process and attendant chemistry. The introduction outlines and highlights the findings and conclusions of the twelve preceding technical reports spanning the period beginning September 1, 1977 and ending March 30, 1984.
The body of this report presents the accumulation of work not yet collected into manuscripts for publications but which will be published within the

the 1984-85 year hence. Included are the aerosol fluorinations of pivalyl, butyryl, isobutyryl and chloroacetyl acid chlorides producing analogous perfluorinated acid fluorides, in good to excellent yields. The aerosol fluorinations of polychloroalkanes produce perfluorinated polychloroalkanes in good to excellent yields however intramolecular 1,2-chloride shifts occur predictably and consistent with the known properties of alphahalo radicals. Chlorine loss and fragmentation are minimal. The aerosol fluorinations of chloroalkyl ethers including 2,3-dichloro-1,4-dioxane were successfully demonstrated, however alpha chloroalkyl ethers tend to lose chlorine more readily than beta chloroalkyl ethers. The attempted aerosol fluorinations of esters, alcohols, nitro-alkanes are described as well as the modestly successful fluorinations of methyl ketones which tend to form poor aerosols.

Appendix A lists aerosol fluorination parameters
Appendix B lists compound characterizations
Appendix C lists prior technical reports
Appendix D general distribution list

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Introduction

This final report of contract No. N00014-77-C-0685, Task No. NR 053-669 brings to a successful conclusion the Office of Naval Research sponsored development of the aerosol direct fluorination process and the complementary development of the chemistry attendant within that goal. Although the initial proposal included both aerosols and liquid phase dispersed "sols" in concept, from a practical point of view it soon became apparent that gas-suspended "sols", aerosols, presented the best potential for achieving truly noval results.

From the outset (9,1,77) steady developmental progress was made on the process which until the beginning of ONR support had made only "proof of concept" type progress. The first technical report[1] (TR-1, 9-1-78) provided the basis for an initial patent search to substantiate the unique and novel concept of aerosol particulate/gas phase heterogeneous reactions in general and fluorinations in particular. The substantial progress in development during the second year outlined in the second technical report (TR-2, 4-1-80)[2] provided chemical results sufficient for the filing of a patent application on December 6, 1979, which resulted in U.S. Patent 4,330,475 dated May 18, 1982.[3] It was discovered at this time that the submission of TR-1 had precluded foreign patent protection. Despite substantial progress in process development no publications describing the process and its progress had yet appeared in the literature, although Dr. Renk and Dr. Adcock during the substantial "down-times" for reactor-equipment modification successfully published the successful synthesis of F-neopentyl bromide and iodide from material partially obtained from aerosol direct fluorination of neopentane.[4] The project was funded for a second two-year period principally on the basis of its potential and on the commitment of ONR in the support of

"high risk" development. The third technical report (TR-3, 10-1-80)[5] was prepared as the seminal paper for aerosol direct fluorination technology and was published in the Journal of the American Chemical Society.[6] This paper outlines the basic process in detail, demonstrates the ability of the aerosol fluorinator to control the degree of substitution, demonstrates the nonstatistical substitution pattern of sequential fluorine attach on fluorinated neopentanes, demonstrates the lack of hydrogen fluoride solvolysis of acid sensitive functional groups, and demonstrates the great utility of "photochemical finishing", i.e. ultraviolet irradiation induced perfluorination. The lack of solvolysis, we later came to realize, was due in part to the unique, low acidity character of aerosol direct fluorinations.

The relative reactivity of methyl groups toward elemental fluorine, is as follows: $CH_3 > CH_2F > CHF_2 \gg CF_3$. This preferential reactivity, which had long been suspected by many, was clearly demonstrated in an unambiguous manner. This preferential reactivity enabled us to prepare a number of symmetrically fluorinated neopentanes and 2,2-dimethyl-1,3-dioxolanes with single residual hydrogens in various parts of the molecule. We later investigated the ability of the interhalogen compounds BrCl and BrF to selectively brominate these compounds. The results of this study comprise Technical Report No. 7.[7]

At this time we had all realized that the ability of the aerosol fluorinator to semi-independently control reaction time, fluorine concentrations, fluorine concentration gradients, hydrocarbon to fluorine stoichiometry, hydrocarbon throughputs, reaction temperatures and the reactor temperature gradient gave us unique control over the complex set of reactions known as "direct fluorination". We had not at this time fully realized the utility of the photochemical reaction stage in achieving high fluorine utilization

efficiency, 120% of theoretical with neopentyl chloride.[8] Neither had we
optimized parameters nor had we achieved sufficient precision in reaction
mass balances to develop basic operating and chemical data on reaction effi-
ciencies. The diligent efforts of Mrs. Heller-Grossman to control the degree
of mono- and difluorination of 2,4-dimethylpentane and thus determine the
relative reactivities of primary, secondary and tertiary hydrogens to elemen-
tal fluorine quite unexpectedly also showed us that optimum main carrier
flows in the aerosol fluorinator were almost five times the values we had
anticipated or had tried prior to that date.[9] As more nearly optimum flows
were adopted by other members of the group, chemical yields rose dramatically
for all reactions and previously "unsuccessful" fluorinations produced modest
to excellent yields.[9] The precision of our chemical mass balances became
such that the differences between effluent concentration of products and the
uncorrected, input-based yield calculations could be used as a basis for the
determination of optimum physical behavior of the reactant in the reactor
system.[10-14] Furthermore the dilute reaction conditions typical of aerosol
direct fluorinations which isolated the individual substitution steps in the
fluorinations, plus the ability to control the reaction stoichiometry permit-
ted the delineation of the individual reaction pathways and thus obtain mech-
anistic information about the interaction of elemental fluorine with various
functional groups and substituents.[14,15]

Technical Report No. 5 describes the first "dependable" direct fluorina-
tions of ketones to perfluoroketones in modest to good yields.[10] The aerosol
direct fluorinations of 3-pentanone, 3-heptanone and 4-heptanone produced the
analogous perfluoroketones in effluent concentrations of 71%, 59% and 92%
respectively although yields based on hydrocarbon input were 13%, 13% and 23%
respectively. This large disparity is due to unreacted starting material

freezing out at the interface between the aerosol generator and the fluorination reactor. This physical loss of reactant, which can be recovered, is more serious for low melting materials which resist crystallization and tend to freeze on impact with the walls. Thus normal alkanes and hydrocarbons with functional groups which introduce assymmetry in the structure behave less ideally than highly symmetrical structures which crystallize rapidly.[10] The aerosol fluorination of cyclopentanone resulted in good yields (24%) of F-pentanoyl fluoride. No F-cyclopentanone was isolated indicating that ring cleavage is a predominant process here,[10] although later work indicates that F-cyclopentanone is so hygroscopic, forming the nonvolatile α,α-diol hydrate, that if formed it might have been lost.[12] To circumvent the problems with the cyclic ketones, indirect syntheses of F-cyclopentanone and F-cyclohexanone were devised.[12] Aerosol direct fluorinations of methoxycyclopentanone and methoxcyclohexane produced the perfluorinated analogues in high effluent concentrations, 57% and 90% respectively and in 22% and 32% isolated yields.[12] Hydrolyses of these compounds in 100% sulfuric acid at 340° to 360°C produced F-cyclopentanone and F-cyclohexanone in 89% and 82% yields respectively although the percent conversions of 61% and 28% respectively indicated incomplete reaction.[12] The use of protecting groups in direct fluorinations of cycloketones was also investigated.[12] Aerosol direct fluorinations of the ethyleneglycol ketals of cyclopentanone and cyclohexanone produced the perfluorinated analogues in high effluent concentrations of 74% and 76% respectively and in 14% and 12% isolated yields respectively.[12] The very stable perfluorinated ketals could be hydrolysed in 100% sulfuric acid to produce F-cyclopentanone (45% yield, 23% conversion) and F-cyclohexanone (100% yield, 36% conversion).

The aerosol fluorinator has successfully perfluorinated two highly branched ketones.[13] The previously unknown F-pinacolone, F-methyl

F-tert-butyl ketone, was produced in 12% isolated yield. Its low yield,
effluent concentration 23%, reflects the presence of 25% monohydryl,
3-difluoromethyl-F-3-methyl-2-butanone and 12% dihydryl, 3,3-bis(difluoro-
methyl)-F-2-butanone ketones in the effluent.[13] The most interesting finding
was that perfluorination of pivalone, di-tert-butyl ketone, results in an
unusual intramolecular rearrangement occuring after the initial fluorine
substitution. Aerosol fluorination of pivalone results in the formation of
F-2,2,5-trimethyl-3-hexanone. One of the tertiary butyl groups has "pin
wheeled" to form an isobutyl group.[13] We hope eventually to ascertain the
mechanism of this unusual rearrangement.

The aerosol fluorinator has produced the highest (28%) isolated yield of
perfluoroadamantane yet published.[11] The photochemical finishing step was
essential in completing the very difficult penultimate fluorine substitu-
tion. The effluent concentration of F-adamantane was 74.4%; the lower yield
value resulted from the physical retention of imputted starting material at
the aerosol generator-reactor interface and thus it is our expectation that
the final optimum yields in all cases will approach the effluent concentra-
tion values as the system is scaled up and optimum physical properties for
the aerosols are achieved.[11]

The aerosol fluorinator has succeeded in perfluorinating the extremely
acid sensitive orthoesters of carbonic acid.[16] The compounds, F-tetramethyl
orthocarbonate and F-ethylene orthocarbonate represent new compositions of
matter previously unsynthesized by any other method. These stable, very
volatile, compounds represent the beginning members of a whole class of
compound of potential use as specialty fluids.

The continuing search for aerosol fluorination survivable functionality
led as to investigate the fluorination of neopentyl chloride and bromide.[15]

The fluorination of neopentyl chloride produced F-neopentyl chloride in 74%
yield (80% effluent concentration), and established that the alkyl carbon-
chlorine bond is surprisingly stable to both molecular fluorine and photo-
chemically generated atomic fluorine at temperatures of 30°C and below.[15]
Furthermore it was clearly established that alkyl chlorides undergo exclu-
sively radical reactions with elemental fluorine. On the other hand,
neopentyl bromide produces F-isopentane in 63% yield (80% effluent concentra-
tion). Furthermore it was established by a series of reactions at 1,2.5, 4
and 12 to one molar ratios of fluorine to neopentyl bromide that initial
fluorine attack occurs exclusively at bromine likely producing either
neopentyl bromine difluoride which disproportionates to neopentyl cation
followed by rearrangement (and further reaction) or at higher stoichiometries
to neopentyl bromine tetrafluoride which disproportionates to alpha-fluoro
neopentyl cation which then rearranges giving a second reaction pathway
unique from the first.[15] We were able to work out the details of both
pathways from the unique substitution products produced and arrive at two
logical reaction sequences both ultimately leading to F-isopentane.[15]

The aerosol fluorination of alkyl chlorides showed that alkyl C-Cl bonds
are very stable to both molecular and atomic fluorine below 30°C.[14,15]
Technical Report No. 11 documents the repeated failure of other fluorination
methods to successfully achieve preservation of this useful functional group
which can be used for subsequent derivativization producing organometallics,
olefins, alkynes, aromatics, carbenes and ylids.[8,14]

The lack of fragmentation, the high yields and reliability of aerosol
direct fluorination allowed as to document that the fluorination of alkyl
chlorides produces predictable products consistent with the known behavior of
alpha-halo radicals. We were able to show that primary alkyl chlorides

produced their perfluorinated analogues in good to excellent yields. Tertiary alkyl chlorides underwent one or more 1,2-chloride shifts ultimately producing one or more primary, F-alkyl chloride isomers in moderate to high combined yields. Secondary alkyl chlorides underwent partial rearrangement to produce mixtures of two or more isomeric F-alkyl chlorides again in good combined yields.[14] In all of the above reactions effluent concentrations of combined product isomers were quite high; fragmentation and C-Cl bond cleavage were generally quite low.
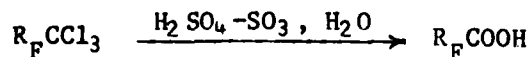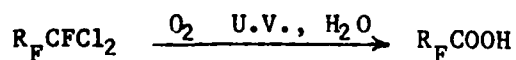
The body of this final technical report collects into a group several groups of experiments which have not as yet been collected into manuscripts but are intergal parts of the theses of Doctors Robin[17] and Evans.[8] Most of this information will eventually be published.
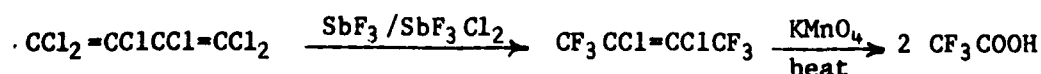
RESULTS AND DISCUSSION

AEROSOL FLUORINATION OF COMPOUNDS WITH SURVIVABLE FUNCTIONALITY

Aerosol Fluorination of Acid Chlorides

The ability to retain a functional group on a hydrocarbon during fluorination, such as an acyl halide, is desirable in many respects. It predetermines the site of functionality and produces the product in a single reaction. Perfluorinated acids can be prepared indirectly by a number of methods analogous to their hydrocarbon counterparts, but these often require several steps. Some examples are the oxidation of chloro-F-alkanes[18,19]

$$R_FCFCl_2 \xrightarrow{O_2 \quad U.V., \quad H_2O} R_FCOOH$$

$$R_FCCl_3 \xrightarrow{H_2SO_4-SO_3, \quad H_2O} R_FCOOH$$

and chloro-F-alkenes[20,21]

$$CCl_2=CClCCl=CCl_2 \xrightarrow{SbF_3/SbF_3Cl_2} CF_3CCl=CClCF_3 \xrightarrow[\text{heat}]{KMnO_4} 2\ CF_3COOH$$

or from additions to fluoro alkenes.[22]

$$CF_3 CF=CF_2 + F_2 CO \xrightarrow[100°]{CsF} (CF_3)_2 CFCOF$$
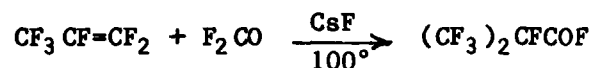
First the appropriate chloro and chlorofluorocarbons must be made before the actual derivation to a carbonyl compound. Th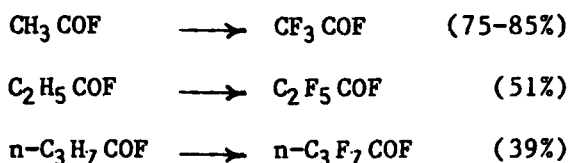ese methods seem overly involved and wasteful of valuable starting materials when electrochemical fluorination can easily produce perfluorinated acid fluorides in good yields from simple acid fluorides[23]

$$CH_3 COF \longrightarrow CF_3 COF \quad (75-85\%)$$
$$C_2 H_5 COF \longrightarrow C_2 F_5 COF \quad (51\%)$$
$$n-C_3 H_7 COF \longrightarrow n-C_3 F_7 COF \quad (39\%)$$

and somewhat poorer yields from acids, esters, aldehydes, and ketones.[24] Electrochemical fluorination in used industrially to produce simple acid fluorides. However, as the length or complexity of the hydrocarbon portion increases, the yields of perfluorinated acid fluorides decrease.

It had been proposed that highly branched hydrocarbons are more difficult to fluorinate, due to the large amount of steric crowding.[3,25] An unsuccessful attempt to fluorinate pivaloyl fluoride with potassium tetrafluorocobaltate (III) seemed to bear this out.[26] However, the LTG fluorination of pivaloyl fluoride in good yield (52%) dispelled this idea. It appeared that the direct fluorination of highly branched structures required more reaction time at higher fluorine concentrations to replace the last remaining hydrogens. Since the aerosol and LTG systems successfully fluorinated highly branched hydrocarbons such as neopentane,[6,27] it was thought that the aerosol fluorination system could similarly fluorinate the highly-branched, and functional pivaloyl chloride.

The LTG system, as well as most other methods, has an acidic environment due to the presence of HF and metal fluorides formed during the fluorination process. In the aerosol fluorination system, the presence of sodium fluoride particles could be viewed as a more neutral or basic system in comparison to the metal fluorides of the LTG metal packing. Even the neutralization of HF by NaF to form the less acidic sodium bifluoride ($NaHF_2$) would make the aerosol system less acidic.[28] The successful aerosol fluorination of the acid sensitive 2,2-dimethyl-1,3-dioxolane seems to bear this out.[6] The LTG fluorination of acyl halides is limited to the acyl fluorides because of the tendency of the molecules to decarbonylate when the halogen is chlorine or bromine.[27] Thus pivaloyl chloride became a logical candidate to test the ability of the aerosol fluorination system to retain the acid function without first forming the acid fluoride.

Synthesis of F-Pivaloyl Fluoride. The aerosol fluorination of pivaloyl chloride gave 0.76 g of F-pivaloyl fluoride in 73% effluent concentration and 48% yield under high-yield fluorination conditions (Appendix A, Table A-1). This compares quite favorably to the 52% yield produced by the LTG system. Although the chlorine was replaced by fluorine, very little decarbonylation occurred, unlike the LTG reaction. This tends to support the idea that the aerosol system is less acidic than the LTG system. An important advantage was shown in that the more readily available acid chlorides could be used.

An important point to note is that a 3 hour aerosol reaction gave 0.76 g of F-pivaloyl fluoride while a 7 day LTG reaction gave 2.26 g of the same product in approximately the same yield. Thus the aerosol system can produce significantly more functionalized fluorocarbon in high yields in a shorter time period. It should be noted that the only reason the aerosol reaction

was not run longer was that the researcher wanted to run the reaction and
completely separate the products in one day. The aerosol system can
obviously be run longer than 3 hours.

Synthesis of F-Butyryl Fluoride. A 3 mmole/h 3-h aerosol fluorination
run of butyryl chloride gave 1.13 g of F-butyryl fluoride in 80% effluent
concentration and 58% yield. This reaction (Table A-1) was run with a high
main carrier flow of 1000 mL/min helium. The hydrocarbon:fluorine ratio of
1:33 was half that of the high yield pivaloyl chloride run. This shows that
the high yields are due more to a high main carrier flow than high fluorine
flows.

Synthesis of F-Isobutyrl Fluoride. A 3 mmole/h 3-h aerosol fluorination
run of isobutyryl chloride gave 1.03 g of F-isobutyryl fluoride in 75%
effluent concentration a 53% isolated yield based on input. The reaction
conditions (Table A-1) are similar to those for the butyryl chloride
reaction.

Aerosol Fluorination of cyclopropyl carbonyl chloride. The aerosol
fluorination of cyclopropyl carbonyl chloride produced no isolated products
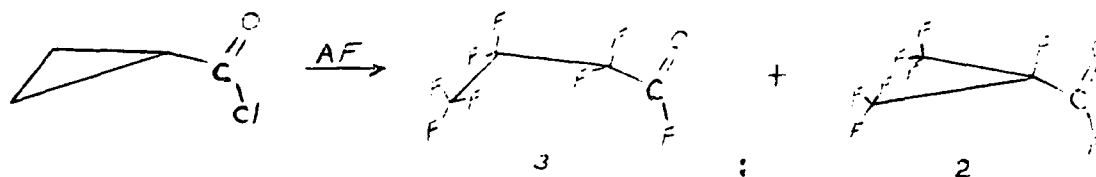
with an intact ring structure. However, of the mixtures collected, a few
were thought to contain minor amounts of one or more partially fluorinated
ring structures due to the large ^{19}F NMR coupling constants (250 Hz) for
peaks in the -100 to -140 ppm range. The perfluorinated ring opened products
for several reactions were F-butyryl fluoride and F-iso-butyryl fluoride in a
3:2 ratio.

Synthesis of F-chloroacetyl Fluoride. Aerosol fluorination of chloro-
acetyl chloride gave F-acetyl fluoride and chloro-F-acetyl fluoride in 20%

$$ClCH_2-C{\overset{O}{\underset{Cl}{}}} \longrightarrow CF_3-C{\overset{O}{\underset{F}{}}} + ClCF_2-C{\overset{O}{\underset{F}{}}}$$
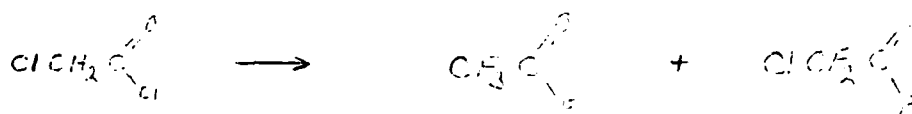
and 34% yields respectively. The acyl chlorine was always replaced by a
fluorine whereas the other chlorine was more resistant to replacement.
Chloro-F-acetyl derivatives have been made in 19% yield by fluorination of
methyltrichloroacetate with SbF_3,[31] in 31% yield by electrochemical fluorina-
tion of chloroacetyl fluoride,[32] and in 77% yield by oxidation of chlorotri-
fluoroethylene.[33] These reactions show that replacement of hydrogen by
fluorine occurs more readily than replacement of alkyl chlorine. The sodium
salt of chloro-F-acetic acid has been shown to be a good source of difluoro-
carbene.

Aerosol Fluorination of Alkyl Chlorides

The direct fluorination of alkyl chlorides is valuable in several
respects. Alkyl chlorides can easily be obtained with one or more chlorines
in desired positions. Hydrogens are replaced in preference to those
chlorines by fluorine in the aerosol system. This was shown in the aerosol
fluorination of $ClCH_2COCl$ and in the many examples of chloroalkanes.[14] Many
of the perfluorinated alkyl chlorides produced by the aerosol system cannot
be easily made by other methods.

Early attempts at direct fluorination of chloroalkanes often gave
mixtures of many chlorofluoro compounds.[29,34-40] Many of these compounds
contained more chlorines than the starting materials. For example in a more

recent publication, Schmeiser, et al.[41] attempted a direct fluorination of 1,2-dichloropropane to synthesize 1,2-dichloro-F-propane from which they expected to produce F-propene. The reaction was conducted at 100–200°C and produced a complex mixture of products, some of which contained 3 or 4 chlorines. The product mixture demonstrated that free chlorine was formed under the reaction conditions and that chlorination as well as dimerization occurred.

Electrochemical fluorination of chloroalkanes also showed the same marginal stability of the alkyl carbon-chlorine bond towards fluorination. For example, electrochemical fluorination of 1,2-dichloroethane produced fluorinated mono-, di- and tri-chloroethanes.[42]

In the indirect fluorination methods, chlorines are replaced in preference to hydrogens. Complete fluorination of highly chlorinated materials to only one or two remaining chlorines is difficult and often requires extreme conditions. The mono- and di-chloro compounds obtained are often secondary chlorides, as these have lower reactivity towards fluorination.[43] However, predicting the position of the last remaining chlorine is not easy nor accurate.

Chloro-F-alkanes can be made from perfluorinated compounds. For example, salts of perfluorocarboxylic acids are converted to chlorides by $ClOSO_2F$.[44,45] The silver salts are also converted by a Hunsdiecker type of reaction.[46-49] Perfluoroalkyl iodides and hydrides are easily chlorinated.[50-52] Perfluoroketones can be converted to gem-dichlorides by PCl_5.[53] Perfluorinated alkanes can be thermally decomposed by chlorine at 900°C into smaller fragment chloro-F-alkanes.[54] Chlorine and hydrogen chloride can also be added across the double bond of F-alkenes.[55,56]

The unsuccessful fluorination of 1,2-dichloroethane by Schmeiser, et al.[41] was probably the result of the high temperatures used. The success of

the aerosol fluorination reactions was likely due to a combination of the low temperatures, the low fluorine concentration, the extremely low free chlorine concentration (if any), and the short reaction times. Thus hydrogens were preferentially replaced by fluorine, and if some some small amount of free chlorine was formed, the reaction conditions did not favor chlorination.

Aerosol Fluorination of Monochloroalkanes.[14],[15] The fluorination of neopentyl chloride showed the stability of an alkyl chlorine substituent towards fluorination. Only 18% of the 2.56 g collected products had no chlorine, while 79.6% was F-neopentyl chloride.[15] There was no rearrangement of the carbon skeleton. This implies that there was no formation of a carbocation, since neopentyl structures are susceptible to carbocation rearrangement,[57] but not to radical rearrangement.[58] Thus the fluorination process probably occurs by a free radical mechanism. There were no products observed which contained more than one chlorine. However, predictable 1,2-chloride shifts were observed during the fluorination of tertiary and secondary alkyl chlorides.[14]

Aerosol Fluorination of Dichloroalkanes. The aerosol fluorination of 1,2-dichloroethane produced 1,2-dichloro-F-ethane with an effluent concentration of 90% and in a 79% yield. This is quite an improvement over the lower yields obtained by other methods. This reaction gave only the 1,2-dichloro-F-ethane isomer. No 1,1-dichloro-F-ethane was observed. Thus the


(1)

(a)   (b)
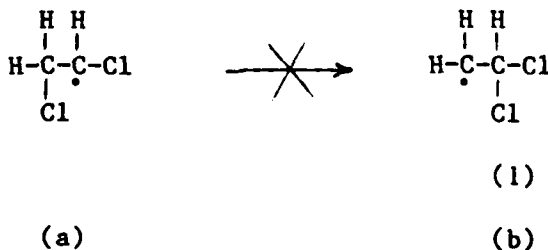
rearrangement shown *above* probably did not occur. A primary to primary radical rearrangement might occur for monochloroethane similar to that

observed for secondary radicals (next page). However, since this does not happen in the above reaction, the initially formed radical (a) must be more stable than the rearranged primary radical (b). This implies that the attached chlorine stabilizes the radical (a). Freidlina has reviewed several chlorine rearrangements in which radicals are stabilized by attached chlorines.[59] Thus radical (a) may be closer in stability to a secondary radical and thus rearrangement to a primary radical is not favored.

The aerosol fluorination of 1,2-dichloro-2-methylpropane produced a 90% effluent concentration of 1,3-dichloro-F-2-methylpropane as the only perfluorinated dichloride in 63% yield. This showed once again that a tertiary chlorine rearranges to a primary position, while a primary chlorine does not rearrange. Since no 1,1-dichloro-F-2-methylpropane was found, this implies either that the initial fluorine attack is directed away from the chlorine to the unhalogenated methyl groups, or that the rearrangement producing a gem-dichloro is not competitive.

The aerosol fluorination of 1,3-dichloropropane was uneventful in producing 1,3-dichloro-F-propane in 80% effluent concentration and 45% yield. As might be expected, the primary chlorines did not rearrange to a secondary position.

The aerosol fluorination of 1,2-dichlorocyclopentane gave four dichloro-F-isomers in 38% total yield (10%, 9%, 10%, 9% respectively).

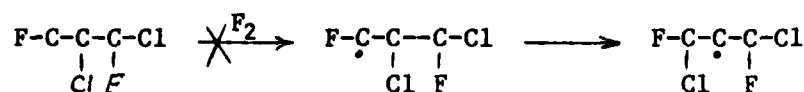trans-1,2   cis-1,2   trans-1,3   cis-1,3
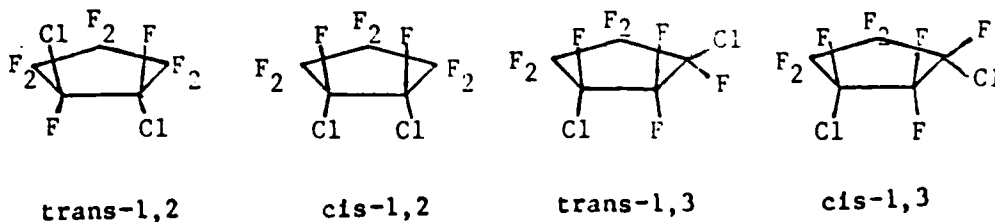
This shows that secondary chlorides can rearrange to other secondary positions. It also shows that cis/trans isomerization occurs as might be

expected in a free radical process.

Aerosol Fluorination of Geminal Dichloroalkanes. The aerosol fluorination of geminal dichloroalkanes provided the opportunity to further study the stability of chlorine stabilized radicals. The aerosol fluorination of 1,1-dichloropropane produced a 1:1 ratio of 1,1-dichloro-F-propane and 1,2-dichloro-F-propane as an inseparable mixture. This suggests that the chlorine stabilized radical (d) has about the same stability as the initially

$$
\begin{array}{ccc}
\text{C-C-C-Cl} & \longrightarrow & \text{C-C-C-Cl} \\
\overset{\displaystyle |}{\underset{\displaystyle Cl}{}} & & \overset{\displaystyle |}{\underset{\displaystyle Cl}{}} \\
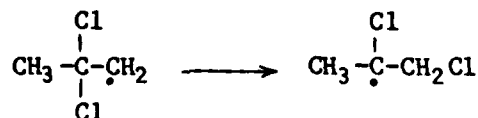(c) & & (d)
\end{array}
$$

formed secondary radical (c). Further migration might be possible, but would not be expected as the terminal methyl carbon would be statistically likely to already have been fluorine substituted before the initial chlorine shift. This would tend to inhibit a second fluorine attack and formation of a

$$
\begin{array}{ccccc}
\text{F-C-C-C-Cl} & \overset{F_2}{\cancel{\longrightarrow}} & \text{F-C-C--C-Cl} & \longrightarrow & \text{F-C-C-C-Cl} \\
\overset{|\ |}{Cl\ F} & & \overset{|\ |}{Cl\ F} & & \overset{|\ |}{Cl\ F}
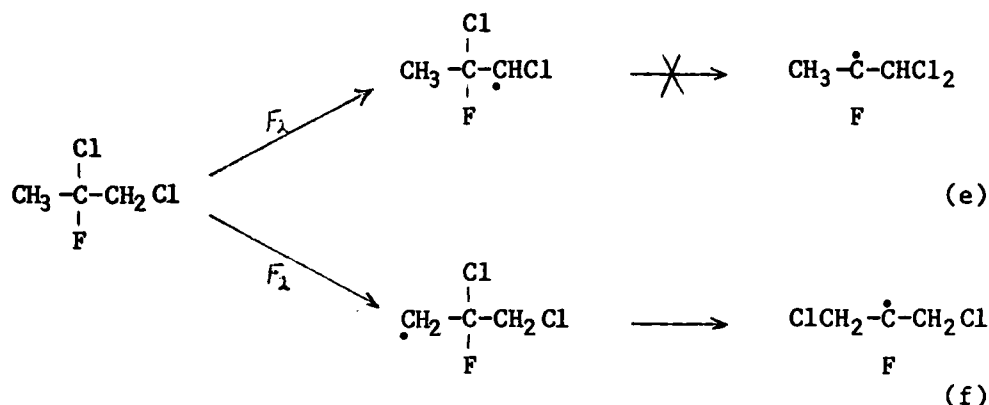\end{array}
$$

radical.

In the aerosol fluorination of 2,2-dichloropropane, initial attack by fluorine can only occur on the terminal methyl hydrogens, forming a primary radical on either terminal methyl group.

$$
\begin{array}{ccc}
\overset{\displaystyle Cl}{\underset{\displaystyle |}{}} & & \overset{\displaystyle Cl}{\underset{\displaystyle |}{}} \\
CH_3-C-CH_2 & \longrightarrow & CH_3-C-CH_2Cl \\
\overset{|}{Cl} & & \overset{|}{C}
\end{array}
$$

If the chlorine atom stabilizes the radical as presumed, then migration of chlorine would be equivalent to a primary to tertiary radical rearrangement. This rearrangement evidently occurs completely in the same manner the tertiary chloride rearrangement since no 2,2-dichloro-F-propane was found. The major products obtained in 26% combined yield were 1,2-dichloro-F-propane and 1,3-dichloro-F-propane in a 2:3 ratio. This is the statistically

expected result if the next fluorine attack could be on either terminal carbon.

$$CH_3-\underset{\underset{F}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_2Cl \quad \xrightarrow{F\cdot} \quad CH_3-\underset{\underset{F}{|}}{\overset{\overset{Cl}{|}}{C}}-\overset{\bullet}{C}HCl \quad \xrightarrow{\quad\not\rightarrow\quad} \quad CH_3-\overset{\bullet}{\underset{F}{C}}-CHCl_2 \qquad (e)$$

$$CH_3-\underset{\underset{F}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_2Cl \quad \xrightarrow{F\cdot} \quad \overset{\bullet}{C}H_2-\underset{\underset{F}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_2Cl \quad \longrightarrow \quad ClCH_2-\overset{\bullet}{\underset{F}{C}}-CH_2Cl \qquad (f)$$
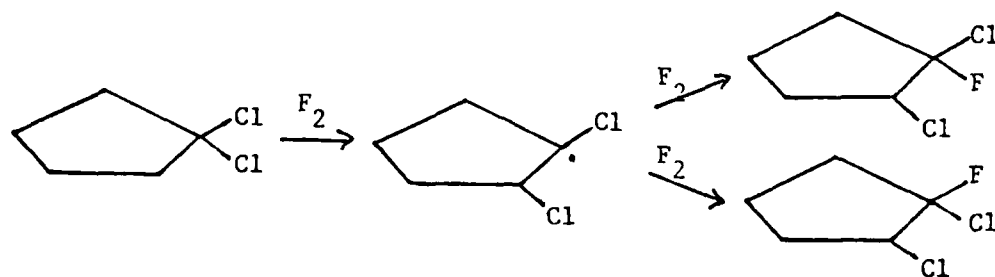
Rearrangement to give the dichloro radical (e) did not occur as no 1,1-dichloro-F-propane was found. Recall that incomplete reverse rearrangement did occur for the fluorination of 1,1-dichloropropane. It seems likely that kinetic not thermodynamic factors are important in this case. No problems exist for a chlorine migration to the opposite carbon, which is statistically more likely to be attacked by fluorine forming a primary radical that could rearrange by a 1,2-chloride shift to the more stable tertiary-like radical (f).

The aerosol fluorination of 3,3-dichloropentane gave four dichloro-F-pentane isomers as major products: 1,3-dichloro-F-pentane; 1,4-dichloro-F-pentane; 2,3-dichloro-F-pentane; and 2,4-dichloro-F-pentane. These products were isolated as an inseparable mixture and tentatively identified by ^{19}F NMR. These products could be formed by very few chloride shifts similar to the chloride shifts in 3-chloropentane.
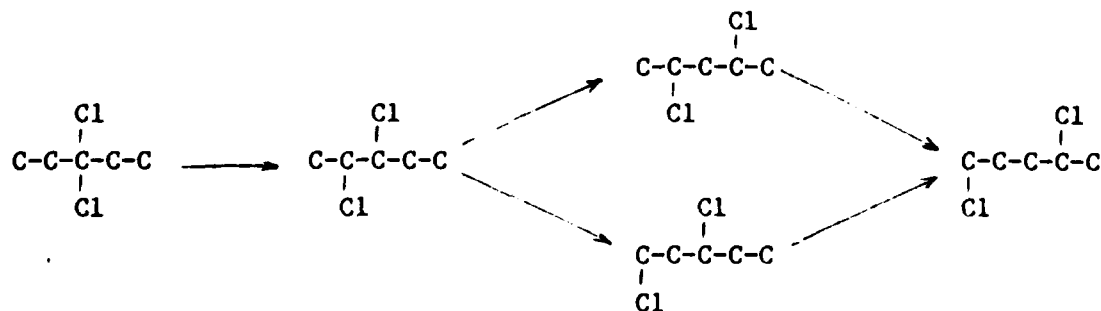
Aerosol fluorination of 1,1-dichlorocycopentane gave a mixture of isomers similar to the mixture produced from trans-1,2-dichlorocyclopentane, namely the perfluorinated trans-1,2-; cis-1,2-; trans-1,3-; and cis-1,3-dichlorocyclopentanes. No 1,1-dichloro-F-cyclopentane was produced. Initial fluorination adjacent to the gem-dichloride carbon would result in a chloride shift giving a tertiary-like radical. This would rearrange to either a cis or trans 1,2-dichloride. Both of these products could rearrange further to

give the cis or trans 1,3-dichlorides. Thus complete scrambling of the chlorine groups results as would be expected for a free radical process.

Aerosol fluorination of 1,1-dichloroneopentane gave 1,1-dichloro-F-neopentane. No rearrangement was observed. Chlorine shifts were blocked by the adjacent quarternary carbon. No 1,3-chloride shifts were observed, indicating that 1,3-shifts are two sequential 1,2-shifts. However, the yields were not high, 26% 1,1-dichloro-F-neopentane and 24% 1-chloro-F-neopentane. This indicated that it is easier to remove a chlorine from a $CHCl_2$ group than from a CH_2Cl. This is similar to the stability of chlorines noted for the Swarts reaction.[60]

The aerosol fluorination of 1,1,1-trichloroethane gave 1,1-2-trichloro-F-ethane in 77% yield. Initial fluorination gives a primary radical. A

$$\overset{\cdot}{C}H_2-CCl_3 \longrightarrow CH_2Cl-\overset{\cdot}{C}Cl_2$$

chlorine shift gives a more stable tertiary-like radical. It should be noted that the CCl_3 group was not stable with respect to rearrangement, but that it was stable to carbon-chlorine bond cleavage.
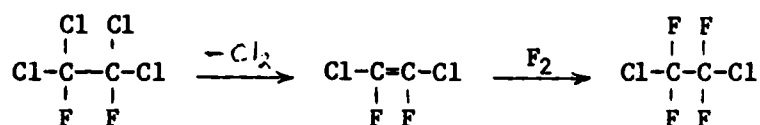
The aerosol fluorination of 1,1,2,2-tetrachloroethane gave 1,2-difluoro-1,1,2,2-tetrachloroethane in 50% yield. The initial fluorination would give a tertiary-like radical. A chloride shift would give a less stable secondary-like radical:

$$\overset{\cdot}{C}Cl_2 - CHCl_2 \quad \overset{\times}{\longrightarrow} \quad CCl_3 - \overset{\cdot}{C}HCl$$
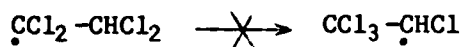
which apparently does not occur.

In summary the chlorine and radical rearrangements for the dichloroalkanes are the same as those observed for the monochloroalkanes.[14] The geminal dichlorides are quite susceptible to free radical rearrangement. A migration of a chlorine from a terminal geminal group leaves a fairly stable secondary-like radical, while migration of a chlorine from a non-terminal geminal group or a trichloromethyl group leaves behind a very stable tertiary-like radical. Thus geminal dichlorides are difficult to retain during fluorination. They can only be retained by blocking possible migration sites such as occured with 1,1-dichloroneopentane. Fortunately, perfluoroketones have been successfully prepared with the aerosol fluorination system.[10] These and other F-ketones can easily be converted to geminal dichlorides with PCl_5.[53]

Aerosol Fluorination of Chloroalkenes. Chloroethylenes were subjected to aerosol fluorination to determine the stability of the chlorines and to study the addition of fluorine to the double bond. Tetrachloroethylene gave 1,2-difluorotetrachloroethane in an effluent concentration of 75%, indicating fairly high stability of the attached chlorines to attack by fluorine. No apparent chlorine migration was observed. However the mode of fluorine addition could not be determined from this experiment. A small amount of 1,2-dichloro-F-ethane was observed. This product may have been formed by elimination of Cl_2 from excited 1,2-difluoro-tetrachloroethane followed by addition of fluorine across the double bond.

$$\underset{\underset{F\ F}{|\ \ \ |}}{\overset{\overset{Cl\ Cl}{|\ \ \ |}}{Cl\text{-}C\text{---}C\text{-}Cl}} \xrightarrow{-Cl_2} \underset{\underset{F\ F}{|\ \ |}}{Cl\text{-}C\text{=}C\text{-}Cl} \xrightarrow{F_2} \underset{\underset{F\ F}{|\ \ |}}{\overset{\overset{F\ F}{|\ \ |}}{Cl\text{-}C\text{-}C\text{-}Cl}}$$

This is supported by the lack of any observed trichlorotrifluoroethane which might be expected for a stepwise loss of just one chlorine.

The aerosol reaction proceeds much more cleanly than a similar reaction carried out in CCl_2F_2 solution at $-80°C$ which gave only 25% yield of 1,2-difluoro-tetrachloroethane.[29] Addition of chlorine to the double bond, dimerization, and significant cleavage of the C—C bond were not observed in contrast to the solution reaction.[29]

The aerosol fluorination of both cis- and trans-1,2-dichloroethylene gave 1,2-dichloro-F-ethane as the major product. The chlorines were stable to fluorine attack. No chloride migrations were observed. The mode of fluorine attack could not be determined from the perfluorination reactions. Partial fluorination seems to indicate that fluorine adds across the double bond before attacking the hydrogens. However, this could not be definitely established because of the difficulty in accurately controlling the aerosol fluorination parameters with the minibubbler. Also, more suitable compounds, as well as purer compounds, would give better data on this question.

Aerosol Fluorination of Chlorinated Ethers. Aerosol fluorination of 2,3-dichloro-1,4-dioxane gave a mixture of cis and trans-2,3-dichloro-F-1,4-dioxane in 21% yield, 2-chloro-F-1,4-dioxane in 35% yield and F-1,4-dioxane in 20% yield. This showed that chloro ethers could be fluorinated directly and still retain the desired chlorine. The same dichloro-F-dioxane was synthesized in several steps by Coe, Dodman, and Tatlow.[30]
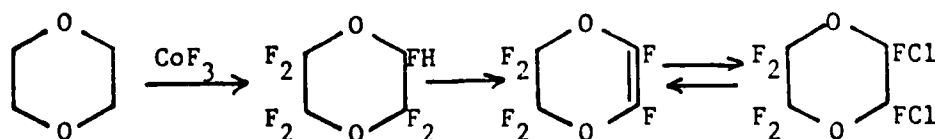
Their initial fluorination of 1,4-dioxane with CoF$_3$ gave a complex mixture, of which the monohydryl compound was isolated in low yield. Drastic conditions were necessary to form the F-dioxene (fused KOH at 150°C) in low yields. The F-dioxene was easily chlorinated to the dichloro-F-dioxane. However the dichloro-F-dioxane once formed is easily converted back to the F-dioxene. Thus the aerosol fluorination system can produce a chloro-perfluoro ether which can then be easily derivatized. However, chlorines are more easily lost due to the presence of an adjacent oxygen atom which can stabilize the radical formed. Thus the yield of dichloro-F-dioxane is lower than the yield of F-dioxane produced from the aerosol fluorination of dioxane.[8]

The aerosol fluorination of 2,2'-dichloro-diethyl ether produced 2,2'-dichloro-F-diethyl ether in a better yield (54%) in comparison to

$$CH_2ClCH_2OCH_2CH_2Cl \longrightarrow CF_2ClCF_2OCF_2CF_2Cl$$
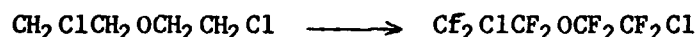
dichloro-F-dioxane. The reduced C-Cl bond cleavage is likely due to the chlorines not being on the carbon atoms adjacent to the oxygen atoms.

Aerosol Fluorination of Esters

Unlike the LTG reaction,[61] esters did not survive aerosol fluorination. The major products obtained from both ethyl-3-chloropropanoate and isopropyl-propanoate were F-propanoyl fluoride and F-acetyl fluoride. Small amounts of fluoroxy compounds were observed. Some F-propane was also produced from the isopropylpropanoate reaction. This failure is likely due to the large amount of free fluoride ion in the aerosol process which is known to catalyse F-ester-F-acid fluoride equilibria.[62] It may be possible to fluorinate esters if fluoride ion could be eliminated by use of compounds such as NaBF$_4$ for aerosol production.

Aerosol Fluorination of Alcohols

The aerosol fluorination of alcohols resulted in extensive cleavage of

the hydroxy group and of the adjacent C-C bond producing F-alkanes. Consid-

erable amounts of F-acid fluorides were also produced. Since fluoroxy

compounds were also produced, these reactions were not extensively worked

up. Tert-butyl alcohol produced a small amount of F-propanone, most likely

by cleavage of a methyl group.

Aerosol Fluorination of Nitroalkanes

The aerosol fluorination of nitropropane resulted in complete cleavage

of the nitro group. The two major products produced were F-propane and NO_2.

This is not unexpected as nitro groups are easily cleaved and the resulting

NO_2 radical is quite stable.

Aerosol Fluorination of Ketones

Synthesis of F-2-Heptanone. Due to the low volatility of 2-heptanone,

sufficient throughputs were not possible employing the basic aerosol fluori-

nation system. Hence, a modified aerosol fluorination system, which employs

a flash evaporator/sublimator fed by a syringe pump, was employed for the

aerosol direct fluorination of 2-heptanone.[11-13] This system offers several

advantages over the basic system. No cold bath need be maintained as was

needed at the hydrocarbon evaporator device of the basic system, and hence

long reactions can be run with little supervision. In addition, lengthy and

tedious throughput experiments are not required when using the modified

system; only the boiling point of the material (or sublimation point in the

case of solid reactants) need be ascertained and the flash evaporator/sub-

limator set at approximately 20°C above that point. A known volume of

hydrocarbon is then delivered from the syringe pump and the density of the

hydrocarbon allows calculation of the throughput. In the case of a solid

reactant throughputs may be determined in the fashion employed for the case

of the basic system.[6,11] The ability to perform lengthy reactions with

little maintainance using the modified aerosol fluorination system also has the advantage that a single run can be performed with a large enough yield of products to allow their characterization after a single run; in the case of the basic system, relatively non-volatile materials giving room temperature throughputs of less than 2 mmol/hr required either runs of very long duration or multiple experiments before a sufficient amount of product could be accumulated for isolation. The basic system is still valuable, however, for the aerosol fluorination of volatile materials, which would boil out of the syringe set-up of the modified system.

The major products from the aerosol fluorination of 2-heptanone were F-2-heptanone and F-n-pentanone which constituted 55% and 26% of the total products collected by weight, respectively. Without correcting for unreacted or partially reacted materials, the percent yield of F-2-heptanone based on the amount of 2-heptanone injected was 8%. As has been noted in the previous aerosol direct fluorinations, the major fragmentation product is usually that resulting from cleavage of the bonds alpha to the carbonyl group. As the ketone being fluorinated becomes more unsymmetrical, it is likely to form a poorer aerosol as previously discussed. Hence as the ketone becomes increasingly unsymmetric, one might expect a higher degree of fragmentation to occur in the aerosol direct fluorination process due to an increasingly poorer aerosol being formed. This seems to be born out by the results of the aerosol direct fluorinations of 4-heptanone, 3-heptanone, and 2-heptanone. In the aerosol fluorination of 4-heptanone virtually no fragmentation products are found, 9% of the products in the fluorination of 3-heptanone are due to alpha cleavage, and 26% of the products in the fluorination of 2-heptanone are due to alpha cleavage.

Only a single previous synthesis of $\underline{F}$-2-heptanone appears in the literature. $\underline{F}$-2-Heptanone was prepared in a 95% yield from the action of antimony pentafluoride on ω-chloroperfluoro-1-heptene epoxide.[63] The chloroperfluoro-1-heptene epoxide is not readily available however, but is synthesized in an eight step reaction sequence starting with ω-hydrylperfluorononanoic acid.

$\underline{F}$-2-heptanone was identified from its infrared spectrum, electron-impact and chemical ionization mass spectra, and ^{19}F nmr spectrum.

The infrared spectrum of $\underline{F}$-2-heptanone exhibits a carbonyl stretch at 1790 cm^{-1} (identical to literature value[63]) and strong absorptions in the 1400 to 1000 cm^{-1} region due to C-F stretches.

The chemical ionization mass spectrum exhibited a top mass peak at m/e = 366, corresponding to the molecular ion and confirming the molecular formula $C_7F_{14}O$. Peaks at m/e = 131, 97, and 69 were also present, corresponding to the $C_3F_5^+$, $C_2F_3O^+$, and CF_3^+ fragments, respectively. The electron-impact mass spectrum exhibited peaks at m/e = 269 and 97, corresponding to the fragments $C_5F_{11}^+$ and $C_2F_3O^+$, respectively, resulting from cleavage of the bonds alpha to the carbonyl group. Other peaks consistent with the structure of $\underline{F}$-2-heptanone were present at m/e = 131, 119, 100, and 69, corresponding to the fragments $C_3F_5^+$, $C_2F_5^+$, $C_2F_4^+$, and CF_3^+, respectively.

The ^{19}F nmr spectrum of $\underline{F}$-2-heptanone agreed with that appearing in the literature,[63] and consisted of five complex multiplets of relative intensity 3:3:2:4:2 at ϕ = -75.17, -81.30, -118.63, -122.67, and -126.67 ppm ($CFCl_3$ internal standard), respectively. The peaks at ϕ = -75.17 and -81.30 ppm are due to the CF_3 groups attached to the carbonyl group and perfluoroalkyl group, respectively. The peaks at ϕ = -118.63, -122.67, and -126.67 ppm correspond to the alpha, beta plus gamma, and delta CF_2 groups, respectively. The beta and gamma CF_2 groups occupy similar environments and hence

occur at approximately the same field, leading to a complex multiplet centered at ϕ = -122.67 ppm.

Synthesis of F-2-Butanone. The major product from the aerosol fluorination of 2-butanone was F-2-butanone, which consitituted 20% of the total products collected by weight; without correcting for unreacted or partially reacted materials, the percent yield of F-2-butanone based on the amount of 2-butanone injected was 9%. The remainder of products were unreacted or partially reacted materials, as ascertained by infrared assay of the complex mixture. The isolation of such a large amount of partially fluorinated materials may be due to 2-butanone forming a poor aerosol as would be the case if 2-butanone were to dissolve the NaF preaerosol. In such a case droplets large enough to settle out in the reactor could form, and the unfluorinated or partially fluorinated materials would be condensed within the reactor. Upon warming of the reactor to ambient temperature following the reaction unless the product trap is removed, these materials would collect in the product trap with the perfluorinated materials.

F-2-Butanone was first produced in poor yields via the direct fluorination of 2-butanone by Bigelow.[64] F-2-butanone has also been synthesized via the action of antimony pentafluoride on 4-chloroperfluoro-1-butene epoxide[63] or F-2-butene epoxide[65] and by the reaction of F-2-(fluorosulfato)butane with cesium or potassium fluoride.[66]

F-2-butanone was identified from its infrared spectrum, electron-impact and chemical ionization mass spectra, and ^{19}F nmr spectrum.

The infrared spectrum agrees with that appearing in the literature,[66] and exhibits a carbonyl stretch at 1790 cm^{-1} and strong absorptions in the 1400 to 1000 cm^{-1} region due to C-F stretches.

The chemical ionization mass spectrum exhibits a top mass peak at m/e = 217, corresponding to the molecular ion plus hydrogen, and a peak at m/e = 197 corresponding to the molecular ion minus fluorine, confirming the molecular formula C_4F_8O. Additional peaks occur at m/e = 147, 97, and 69, corresponding to the fragments $C_3F_5O^+$, $C_2F_3O^+$, and CF_3^+, respectively. The electron-impact spectrum exhibited peaks at m/e = 147, 119, 97, and 69 corresponding to the fragments $C_3F_5O^+$, $C_2F_5^+$, $C_2F_3O^+$, and CF_3^+, respectively, consistent with the structure of F-2-butanone.

The ^{19}F nmr of F-2-butanone consists of three peaks of relative intensity 3:3:2 at $\emptyset$ = -75.30, -82.28, and -122.11 ppm ($CFCl_3$ internal standard), respectively. The peak at $\emptyset$ = -75.30 ppm corresponds to the CF_3 group attached to the carbonyl group, and is split into a triplet by coupling with the CF_2 group, which appears at a quartet at $\emptyset$ = -122.11 ppm (J = 8.8 Hz). The peak at $\emptyset$ = -82.28 ppm is assigned to the CF_3 group attached to the CF_2 group and appears at a singlet.

Synthesis of F-Acetone. The major product from the aerosol direct fluorination of acetone was F-acetone, which constituted 48% of the total products collected by weight. Without correcting for unreacted or partially reacted materials the percent yield of F-acetone based on the amount of acetone injected was 4%. Also isolated from the reaction was 1-hydrylperfluoroacetone, which constituted 30% of the total products collected by weight. As discussed for the case of 2-butanone, the isolation of a significant amount of partially fluorinated materials may indicated partial dissolving of the NaF preaerosol by acetone.

The infrared spectrum of F-acetone was identical to that appearing in the literature.[67] F-Acetone is a well characterized material and is available commercially.

1-Hydrylperfluoroacetone, CF_3COCF_2H, exhibits a weak C-H stretch at 2970 cm^{-1} and a carbonyl stretch at 1790 cm^{-1}, in addition to strong absorption in the 1400 to 1000 cm^{-1} region due to C-F stretches. The electron-impact mass spectrum included peaks at m/e = 148 and 129 corresponding to the molecular ion and the molecular ion minus fluorine, respectively, in addition to peaks at m/e = 119, 101, 97, 79, 69, and 51 corresponding to the fragments $C_2F_5^+$, $C_2F_4H^+$, $C_2F_3O^+$, $C_2F_2HO^+$, CF_3^+, and CF_2H^+, respectively, consistent with the structure of 1-hydrylperfluoroacetone. The chemical ionization mass spectrum of 1-hydrylperfluoroacetone exhibited a base peak at m/e = 150, corresponding to the molecular ion plus two hydrogens. The ^{19}F nmr spectrum of 1-hydrylperfluoroacetone consists of a triplet at $\emptyset$ = -76.20 ppm ($J_{CF_3-CF_2}$ = 6.11 Hz) and a doublet of quartets at $\emptyset$ = -129.51 Hz (J_{CF_2-H} = 48.02 Hz) corresponding to the CF_3 and CF_2 groups, respectively. The ^1H nmr consists of a triplet at δ 6.15 ppm.

EXPERIMENTAL

Characterization of Compounds

Workup of products, following removal of hydrogen fluoride, consisted of vacuum line fractionation, infrared assay of fractions, and gas chromatographic separation of materials. Characterization were made by vapor phase infrared spectrophotometry, electron-impact and chemical ionization mass spectrometry, ^1H and ^{19}F nuclear magnetic resonance (nmr) spectroscopy, and elemental analysis. Product distributions and percent yields were determined by gas chromatographic assay (cut and weight method).

Vacuum Line. An all glass vacuum system with Teflon stopcocks (Kontes Scientific Glassware) was employed. A Welch Duo-seal vacuum pump (model 1402B) was used, and all transfers, fractionations, etc., performed at

approximately 3 microns of mercury (Hastings vacuum gauge, model VT-5B).

Gas Chromatography. Gas chromatographic separations were performed on a Bendix model 2300 gas chromatograph (subambient, multicontroller) employing a 7 meter x 3/8" 13% Fluorosilicone QF-1 (Analabs) stationary phase on 60-80 mesh acid-washed Chromosorb P conditions at 225°C (12 hours) or a 4 meter x 3/8" 10% SE-52 phenylmethyl silicone rubber stationary phase on acid-washed Chromosorb P conditions at 250°C (12 hours). The carrier gas was helium (60 cc/min). Injections were made using standard microliter syringes (Hamilton) or in the case of extremely volatile materials with Precision Sampling Corporation "Pressure-Lok" syringes. All retention times (t_R) were measured relative to the time of injection.

Infrared Spectra. All infrared spectra were recorded as gases in a gas cell (path length 10 centimeters) with potassium chloride optics or as neat liquids between potassium chloride plates. Spectra were recorded on a Perkin Elmer model 1330 infrared spectrophotometer.

Mass Spectra. Mass spectra were taken on a Hewlett-Packard GC/MS (5710A GC, 5980 MS, 5934A computer); electron-impact mass spectrometry was performed at 70 eV and chemical ionization mass spectrometry employed a methane plasma.

Nuclear Magnetic Resonance. ^{1}H and ^{19}F nmr spectra were taken with a JEOL FX90Q (omniprobe) nmr spectrometer operating at 89 MHz for ^{1}H and 84 MHz for ^{19}F. Spectra were recorded with tetramethylsilane (TMS) as internal standard for ^{1}H and in $CDCl_3$ with 1% $CFCl_3$ internal standard for ^{19}F.

Elemental Analysis. Elemental analysis were performed by Schwarzkopf Microanalytical laboratory, Woodside, New York.

Aerosol Fluorination Reactions

Typical Reaction Procedures

Before a reaction was started with the unmodified aerosol fluorinator,[6]

the hydrocarbon throughputs were determined. From appropriate vapor pressure data, hydrocarbon reservoir temperatures were established. Temperatures which produced 10 to 40 mm partial vapor pressure were found to produce suitable throughputs. Throughputs were determined by trapping and weighing the hydrocarbon for a certain time period before it entered the aerosol generator. This procedure was eliminated by the calibrated syringe pump modification.[11-13]

Before a new compound was fluorinated, the reactor modules and aerosol generator were cleaned, the NaF trap was renewed, and fresh NaF was added to the nickel boat in the oven. The NaF in both the oven and the HF trap needed to be renewed after 4 runs. The oven was heated while maintaining a low helium flow until it reached operating temperatures of 800-850°C. As this required about 2 hours, throughputs were often determined at that time.

Once the oven reached operating temperatures and a desired throughput was known, all appropriate helium flows were turned on to approximately half the reaction values. At this time cooling of the reactor system commenced. Before the desired temperatures were reached, fluorine was introduced into the reactor modules. This passivated the reactor surfaces if they had been exposed to the atmosphere. Also any organic material remaining in the reactor was fluorinated and removed without contaminating that run. Final fluorine flow settings were then set according to the desired degree of fluorination. A setting of 1 mL/min delivers 2.44 mmole/hr of fluorine. If perfluorination was desired, 2 to 3 fluorine molecules were introduced for every hydrogen present. This usually gave 3 to 4% fluorine concentration in the last stage.

If the photochemical stage was used, the U.V. lamp and its cooling water were turned on 10 minutes before the hydrocarbon flow was started. Hydrocarbon was introduced as long as desired. This was usually about four hours.

Any drop in the flows indicated the system was partially blocked. This usually occurred in the NaF trap if it was not renewed frequently. Fluorine and hydrocarbon flows could be stopped temporarily while the trap was renewed. A blockage elsewhere is more serious and requires complete shut down.

Shutting down the system is in the reverse order of start up with the exception of the oven which is turned off with the hydrocarbon flow. A low helium flow is maintained as the reactor warms up in order to flush out fluorine and any other materials.

Typical aerosol fluorination reactions for individual compounds are given in the following experimental sections. Details of the aerosol fluorination parameters are tabulated in Appendix A. Compounds are characterized in Appendix B. All reactions are photochemically finished unless otherwise stated.

Pivaloyl Chloride

Trimethylacetyl chloride (Aldrich) (pivaloyl chloride or 2,2-dimethyl-propanoyl chloride) has a vapor pressure at 0°C such that a helium flow of 60 mL/min through the sparge tube of the hydrocarbon evaporator produces a throughput of 0.24 g/h (2.0 mmol/h Table A-1). A 3 hour photochemically finished run produced 1.05 g of crude product after fractionation on the vacuum line. Separation of this material by gas chromatography on the SE-52 column (0°C/5 min; 25°C/min to 100°C/5 min; 25°C/min to 200°C/25 min) gave a 0.76 g F-pivaloyl fluoride (48% yield) at t_R 4 min. (Table B-1).

Butyryl Chloride

Butyryl chloride was prepared by dropping $SOCl_2$ (Fischer) into ice-cold butyric acid (Eastman), refluxing at 70°C, and fractionally distilling the solution. Butyryl chloride has a vapor pressure at 23°C such that a helium

flow of 30 mL/min produces a throughput of 0.27 g/h (3.0 mmol/h). A 3 hour run produced 1.41 g of crude product after fractionation on the vacuum line. Separation on the QF-1 column (0°C/5 min; 10°C/min to 40°C/4 min; 25°C/min to 180°C/10 min) gave 80% $\underline{F}$-butyryl fluoride t_R = 11 min, in 58% yield of the theoretical throughput. It is characterized in Table B-1. The aerosol fluorination parameters are given in Table A-1.

Iso-Butyryl Chloride

Iso-butyryl chloride (Aldrich) has a vapor pressure at 23°C such that a helium flow of 24 mL/min produces a throughput of 0.32 g/h (3.0 mmol/h). A 3 hour run (Table A-1) produced 1.37 g of crude product after fractionation on the vacuum line. Separation on the QF-1 column (0°C/5 min; 10°C.min to 40°C/4 min; 25°C/min to 180°C/10 min) gave 75% $\underline{F}$-iso-butyryl fluoride (1.03 g a 53% yield) at t_R = 10 min. Characterization is given in Table B-1.

Cyclopropyl Carbonyl Chloride

Cyclopropyl carbonyl chloride was prepared from cyclopropyl carboxylic acid and $SOCl_2$ by the method of Dadson and Minta.[68] Cyclopropyl carbonyl chloride has a vapor pressure at 22°C such that a helium flow of 23 mL/min produces a throughput of 0.19 g/h (1.8 mmol/h). A 2.5 hour run produced 0.5833 g of crude product after fractionation on the vacuum line. Separation on the QF-1 column (0°C/5 min; 10°C/min to 60°C/0 min; 25°C/min to 180°C/10 min) gave 13% $\underline{F}$-isobutyryl fluoride at t_R = 7.5 min, 20% $\underline{F}$-butyryl fluoride at t_R = 8.5 min and unidentified compounds at t_R = 10 min (7%), 11 min (21%), 15 min (7%) and 16 min (29%). The calculated yields of the two open chain $\underline{F}$-butyl fluorides were 8% and 13% respectively based on the theoretical throughput. The aerosol fluorination parameters for this reaction are given in Table A-1.

Chloroacetyl Chloride

Chloroacetyl chloride was prepared by the addition of $SOCl_2$ to chloro-acetic acid (Eastman). Chloroacetyl chloride has a vapor pressure at 28°C such that a helium flow of 10 mL/min gives a throughput of 0.34 g/h (3 mmol/h). A 3 hour run produced 0.80 g of crude products after fraction on the vacuum line. Purification of the products on the QF-1 column (5°C/5 min; 10°C/min to 75°C/4 min; 25°C/min to 180°C/10 min) gave 26% F-acetyl fluoride (t_R = 4 min) and 51% chloro-F-acetyl fluoride (t_R = 10 min). The calculated yields were 20% and 34%, respectively, based on the theoretical throughput. The aerosol fluorination parameters are given in Table A-1. Characterizations are given in Table B-1.

1,2-Dichloroethane

1,2-Dichloroethane (Fischer) has a vapor pressure at -23°C such that a helium flow of 45 mL/min produces a throughput of 0.20 g/h (2.0 mmol/h). A 2 hour run produced 0.601 g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (0°C/2 min; 5°C/min to 25°C/0 min; 50°C/min to 140°C/6 min) gave 10% 1-chloro-F-ethane (t_R = 3 min) and 90% 1,2-dichloro-F-ethane at 8 min in 79% yield. The aerosol fluorination parameters are given in Table A-10. 1,2-Dichloro-F-ethane is characterized in Table B-1.

1,2-Dichloro-2-Methylpropane

1,2-Dichloro-2-methylpropane (Chemical Samples Co.) has a vapor pressure at 22°C such that a helium flow of 33 mL/min produces a throughput of 0.25 g/h (2.0 mmol/h). A 2 hour run produced 0.731 g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (0°C/5 min; 10°C/min to 30°C/min; 25°C/min to 190°C/10 min) gave 90% 1,3-dichloro-F-2-methylpropane (t_R = 12 min) in 63% yield. The aerosol fluorination parameters are given in Table A-2. This compound is characterized in Table B-2.

Trans-1,2-Dichlorocyclopentane

Trans-1,2-dichlorocyclopentane was prepared by chlorination of cyclo-pentene according to the method of Mousseron, Granger and Valette.[69] It has a vapor pressure at 22°C such that a helium flow of 175 mL/min produces a throughput of 0.14 g/h (1.0 mmol/h). A 3 hour run produced 0.8426 g of crude product after fractionation on the vacuum line. Separation on the QF-1 column (19°C/13 min; 10°C/min to 60°C/15 min; 50°C/min to 180°C/15 min) gave 1% C_4F_{10} (t_R = 5 min.) 6% F-cyclopentane (t_R = 12 min.) 1% $C_5F_{11}Cl$ (t_R = 15 min.), 24% chloro-F-cyclopentane (t_R = 22 min.), a mixture of 10% trans-1,2-dichloro-F-cyclopentane, 10% trans-1,3-dichloro-F-cyclopentane, 9% cis-1,3-dichloro-F-cyclopentane (t_R = 30 min.), and 9% cis-1,2-dichloro-F-cyclopentane (t_R = 31 min.). The calculated yields are the same as the above distribution yields. The aerosol fluorination parameters are given in Table A-3. Characterizations are given in Tables B-3 and B-4.

1,1-Dichloropropane

1,1-Dichloropropane was prepared by addition of propionaldehyde (Eastman) to ice-cold PCl_5 (Aldrich), followed by addition of several portions of water, and by fractional distillation of the organic layer giving 1,1-dichloropropane in 60% yield. It has a vapor pressure of 0°C such that a helium flow of 50 mL/min produces a throughput of 0.42 g/h (3.7 mmol/h). A 2 hour run produced 1.09 g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (-10°C/4 min; 4°C/min to 30°C/1 min; 10°C/min to 90°C/5 min) gave 8% C_3F_7Cl (t_R = 5.5 min.) and 90% of a 1:1 mixture of 1,1-dichloro-F-propane and 1,2-dichloro-F-propane (t_R = 14 min). The combined calculated yield for both compounds is 60%. The aerosol fluo-rination parameters are given in Table A-2. Both compounds are characterized in Table B-1.

2,2-Dichloropropane

2,2-Dichloropropane prepared by the addition of acetone (Fischer) to PCl_5 followed by fractional distillation. The syringe pump of the modified reactor delivered 0.51 mL/hr (2.9 mmol/h) 2,2-dichloropropane to a heated inlet.[11-13] A 1 hour run produced 0.242 g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (-10°C/4 min; 4°C/min to 30°C/1 min; 10°C/min to 180°C/5 min) gave one major peak (85%, t_R = 14 min.) which contained a 2:3 mixture of 1,2-dichloro-F-propane and 1,3-dichloro-F-propane. The aerosol fluorination parameters are given in Table A-4. Both compounds are characterized in Table B-1.

1,3-Dichloropropane

1,3-Dichloropropane, prepared by the addition of $SOCl_2$ to 1,3-propane-diol and pyridine followed by fractional distillation, was delivered by a syringe pump at 0.51 ml/hr (2.9 mmol/h) to a heated inlet. A 4.5 hour run produced 1.71 g of crude product after fractionation on the vacuum line. Separation with the 2,2-dichloropropane GC program gave 70% 1,3-dichloro-F-propane (t_R = 14 min.) in 43% yield. The aerosol fluorination parameters are given in Table A-4; characterization in Table B-1.

3,3-Dichloropentane

3,3-Dichloropentane was prepared by addition of 3-pentanone (Aldrich) to PCl_5. A helium flow of 30 mL/min through mini-evaporator at 28°C produces a throughput of 0.20 g/h (0.7 mmol/h). A 2 hour run period produced 0.185 g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (15°C/5 min; 10°C/min to 75°C/0 min; 25°C/min to 180°C/7 min) gave 58% of a mixture of chloro-F-pentane isomers (t_R = 5.5 min.) and 38% of a mixture of dichloro-F-pentane isomers (t_R = 12.5 min). Four dichloro isomers were tentatively identified as 1,3-di-chloro-F-pentane, 1,4-dichloro-F-pentane, 2,3-dichloro-F-pentane, and 2,4-dichloro-F-pentane. Tentative

^{19}F NMR characterizations of these four isomers are given in Table B-5. The aerosol fluorination parameters are given in Table A-2.

1,1-Dichlorocyclopentane

1,1-Dichlorocyclopentane was prepared by addition of cyclopentanone (Aldirch) to PCl_5. A helium flow of 45 mL/min through the mini-evaporator at 28°C produces a throughput of 0.25 g/h (1.8 mmol/h). A 3-hour run produced 1.0 g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (0°C/5 min; 10°C/min to 60°C/5 min; 10°C/.min to 180°C/10 min) gave 8.6% F-cyclopentane (t_R = 4 min.) 29.7% chloro-F-cyclopentane (t_R = 10 min.) 57.8% of a mixture of four cis/trans 1,2- and 1,3- dichloro-F-cyclopentane isomers (t_R = 18 min.). The calculated yield of chloro-F-cyclopentane is 37% while the combined yield for the dichloro-F-cyclopentane isomers is 20%. The aerosol fluorination parameters are given in Table A-3; characterization B-3,4.

1,1-Dichloroneopentane

1,1-Dichloroneopentane was prepared by addition of trimethylacetaldehyde (Aldrich) to PCl_5. A helium flow of 25 mL/min through the mini-evaporator at 28°C produces a throughput of 0.32 g/h (2.3 mmol/h). A 1.5 hour run produced 0.85 g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (25°C/10 min; 10°C/min to 75°C/10 min; 25°C/min to 160°C/10 min) gave 30% 1-chloro-F-neopentane (t_R = 6 min.) and 34% 1,1-dichloro-F-neopentane (t_R = 16 min.). The calculated yields are 24% and 26% respectively. 1,1-Dichloro-F-neopentane is characterized in Table B-6. The aerosol fluorination parameters are given in Table A-2.

1,1,1-Trichloroethane

1,1,1-Trichloroethane (Eastman) has a vapor pressure at 0°C such that a helium flow of 15 mL/min produces a throughput of 0.25 g/h (1.9 mmol/h). A 2 hour run produced 0.333 g of crude product after fractionation on the vacuum

line. Separation on the SE-52 column (25°C/10 min; 10°C/min to 75°C/10 min; 25°C/min to 160°C/7 min) gave 82.4% 1,1,2-trichloro-$\underline{F}$-ethane (t_R = 14 min.) and 15.7% of 3 unidentified products between t_R = 20-22 min. The aerosol fluorination parameters are given in Table A-5. The calculated yield 1,1,2-trichloro-$\underline{F}$-ethane is 77%, and it is characterized in Table B-1.

1,1,2,2-Tetrachloroethane

1,1,2,2-Tetrachloroethane (Eastman) has a vapor pressure at 28°C such that a helium flow of 70 mL/min produces a throughput of 0.67 g/h (4.0 mmol/h). A 2 hour run produced 1.010 g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (0°C/2 min; 5°C/min to 25°C/min to 180°C/10 min) gave 10% 1,2-dichloro-$\underline{F}$-ethane (t_R = 7 min.) and 80% 1,1,2,2-tetrachloro-$\underline{F}$-ethane (a 50% yield, t_R = 21 min.). It is characterized in Table B-1. The aerosol fluorination parameters are given in Table A-5.

2,3-Dichloro-1,4-Dioxane

2,3-Dichloro-1,4-dioxane was prepared by chlorination of 1,4-dioxane (Fischer) by $SOCl_2$ with U.V. irradiation.[70] A helium flow of 120 mL/min through the mini-evaporator at 75°C produces a throughput of 0.28 g/h (1.8 mmol/h). A 2 hour run produced 0.67% g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (-10°C/6 min; 5°C/min to 60°C/0 min; 20°C/min to 160°C/10 min) gave 24.1% $\underline{F}$-1,4-dioxane (t_R = 4.5 min.) in 20% yield, 45.5% 2-chloro-$\underline{F}$-1,4-dioxane (t_R = 13 min.) in 35% yield, and 29.6% 2,3-dichloro-$\underline{F}$-1,4-dioxane (t_R 23 min.) in 21% yield. The aerosol fluorination parameters are given in Table A-6. Characterizations are given in Tables B-1, B-7, and B-8 respectively.

Bis-(2-Chloroethyl) Ether

Bis-(2-Chloroethyl) ether (Eastman) has a vapor pressure at 28°C such that a helium flow of 140 mL/min produces a throughput of 0.37 g/h (2.6

mmol/h). A 2 hour run produced 1.215 g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (25°C/5 min; 5°C/min to 75°C/5 min; 20°C/min to 180°C/10 min) gave 66.9% bis-(2-chloro-F-ethyl) ether t_R = 7 min in 54% yield. It is characterized in Table B-9. The aerosol fluorination parameters are given in Table A-6.

Tetrachloroethylene

Tetrachloroethlyene (Aldrich) has a vapor pressure at 22°C such that a helium flow of 30 mL/min produces a throughput of 0.35 g/h (2.1 mmol/h). A 2 hour run produced 0.68 g of crude product after fractionation on the vacuum line. Separation on the SE-52 column (0°C/2 min; 5°C/min to 25°C/0 min; 50°C/min to 100°C/10 min) gave 75% distribution of 1,2-difluoro-1,1,2,2-tetrachloroethane in 58% yield. The aerosol fluorination parameters are given in Table A-10; characterization in B-1.

1,2-Dichloroethylenes

A mixture of cis and trans 1,2-dichloroethylenes (Aldrich) was separated gas chromatographically before use. As less than 1 g of each was collected, the mini-evaporator was used. A flow of 10 mL/min carried 0.116 g/h of cis-1,2-dichloroethene and 0.136 g/h of trans-1,2-dichloroethene into the reactor. The major product in each reaction was 1,2-dichloro-F-ethane. The yields were not calculated. The aerosol fluorination parameters are given in Table A-5; characterization in B-1.

Ethyl-3-Chloropropanoate

Ethyl-3-chloropropanoate (Aldrich) has a vapor pressure at 22°C such that a helium flow of 190 mL/min produces a throughput of 0.24 g/h (1.75 mmol/h). A 3 hour run produced a large number of perfluorinated products. These included F-propanoyl fluoride, acetyl fluoride, and carbonyl fluoride. The aerosol fluorination parameters are given in Table A-7.

Iso-Propyl-Propanoate

Iso-propyl-propanoate (Baker) has a vapor pressure at 28°C such that a helium flow of 15 mL/min produces a throughput of 0.44 g/h (3.8 mmol/h). A 2 hour run produced many perfluorinated products. These included F-propanoyl fluoride, F-acetyl fluoride, F-propanone, and a small amount of fluoroxy compounds. The aerosol fluorination parameters are given in Table A-7.

Iso-Amyl Alcohol

Iso-amyl alcohol (Mallinckrodt) has a vapor pressure at 23°C such that a helium flow of 125 mL/min produces a throughput of 0.15 g/hr (1.7 mmol/h). A 3 hour run produced a mixture of F-iso-pentane, F-iso-butane and several F-alkyl acid fluorides. The aerosol fluorination parameters are given in Table A-8.

2-Butanol

2-Butanol (Fischer) has a vapor pressure at 28°C such that a helium flow of 30 mL/min produces a throughput of 0.15 g/h (2.0 mmol/h). A 2 hour run produced a mixture of products containing F-butane, F-propanoyl fluoride, F-acetyl fluoride, carbonyl fluoride, and F-2-butane. The aerosol fluorination parameters are given in Table A-8.

Tert-Butanol

Tert-butanol (Fischer) has vapor pressure at 24°C such that a helium flow of 20 mL/min produces a throughput of 0.28 g/h (3.8 mmol/h). A 1 hour run produced a mixture of F-iso-butane, F-iso-butene, F-acetyl fluoride, carbonyl fluoride, and F-2-propanone. The aerosol fluorination parameters are given in Table A-8.

Nitropropane

Nitropropane (Eastman) has a vapor pressure at 28°C such that a helium flow of 80 mL/min produces a throughput of 0.22 g/h (2.5 mmol/h). A 2 hour

run produced F-propane and NO_2. The aerosol fluorination parameters are given in Table A-9.

Aerosol Fluorination of 2-Heptanone

Due to the low volatility of 2-heptanone, aerosol fluorination utilizing the basic aerosol fluorination system was not possible. At the highest carrier flow allowed with the system, a sufficient throughput (at least 1 mmol/hr) of material was unattainable. Hence, the aerosol fluorination of 2-heptanone was conducted with the syring pump/flash evaporator modified aerosol fluorination system.[11-13] A pump speed corresponding to 3.8 mmol/hr was established and 1.7 ml (12.2 mmol) 2-heptanone delivered over a 3.2 hour period. Details of the aerosol fluorination parameters are given in Table A-11, Appendix A.

Products were transferred to the vacuum line and worked up as described. The contents of the -131°C trap (0.633 g) were collected and separated on the SE-52 gas chromatographic column with the temperature program: 0°C, 2 min; 1°C/min to 10°C; 10°C, 1 min; 20°C/min to 180°C. The major products were F-2-heptanone (t_R = 9 min) and F-n-pentane (t_R = 3.5 min) which constituted 55% (0.348 g, 0.95 mmol) and 26% (0.165 g, 0.57 mmol) of the total products collected by weight, respectively. Without correcting for unreacted or partially reacted materials, the percent yield of F-2-heptanone based on the amount of 2-heptanone injected (12.2 mmol) was 8%. The characterization of F-2-heptanone is given in Table B-10, Appendix B. The ^{19}F nmr spectrum of F-2-heptanone was in agreement with that appearing in the literature.[63] F-n-Pentane was identified from its infrared spectrum.[71]

Aerosol Fluorination of 2-Butanone

The aerosol fluorination of 2-butanone was conducted with the modified aerosol fluorination system. A pump speed corresponding to 3.9 mmol/hr was established and 1.4 ml (15.6 mmol) 2-butanone delivered over a 4 hour

period. Details of the aerosol fluorination parameters are given in Table A-11, Appendix A.

Products were transferred to the vacuum line and worked up as described above. The contents of the -131°C trap (1.553 g) were collected and separated on the QF-1 gas chromatographic column with the temperature program: 0°C, 2 min; 1°C/min to 10°C, 1 min; 20°C/min to 180°C. The major product was F-2-butanone (t_R = 11.5 min) which constituted 20% (0.311 g, 1.44 mmole) of the total products collected by weight. Without correcting for unreacted or partially reacted materials, the percent yield of F-2-butanone based on the amount of 2-butanone injected (15.6 mmol) was 9%. The characterization of F-2-butanone is given in Table B-11, Appendix B. The infrared and ^{19}F nmr spectra of F-2-butanone were in agreement with those found in the literature.[63],[66]

Aerosol Fluorination of Acetone

The aerosol fluorination of acetone was conducted with the modified aerosol fluorination system. A pump speed corresponding to 5.1 mmol/hr was established and 1.5 ml (20.4 mmol) acetone delivered over a 4 hour period. Details of the aerosol fluorination parameters are given in Table A-11, Appendix A.

Products were transferred to the vacuum line and worked up as described above. The -131°C trap contents (0.309 g) were collected and separated on the SE-52 gas chromatographic column with the temperature program: -40°C, 2 min; 1°C/min to -30°C;, 1 min; 20°C/min to 180°C. The major product was F-acetone (t_R = 3.5 min) which constituted 48% (0.148 g, 0.89 mmol) of the total products collected by weight. Without correcting for unreacted or partially reacted materials the percent yield of F-acetone based on the amount of acetone injected (20.4 mmol) was 4%. F-Acetone was identified from its infrared spectrum.[67]

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APPENDIX A

Reaction Parameters

TABLE A-1

Aerosol Fluorination of Acid Chlorides

Run Parameters	1[a]	2	3	4	5
Hydrocarbon Throughput					
mmole/hour	2.0	3.0	3.0	2.0	3.0
He Carrier (mL/min)	65	30	24	25	10
Temperature (°C)	0°	23	23	23	28
F_2 Flow (mL/min)					
Stage 1	20	20	20	20	20
Stage 2	20	20	20	20	–
Stage 3	20	–	20	20	–
He Diluent (mL/min)					
Stage 1	80	80	80	80	120
Stage 2	80	80	80	80	–
Stage 3	80	–	80	–	–
Reactor Temps (°C)					
Aerosol Generator	50	40	40	45	40
Module 1	-45	-40	-45	-40	-45
Module 2	-30	-30	-30	-30	-35
Module 3	20	10	10	10	0
Main He Carrier (mL/min)	1200	1000	1000	1200	1000
Hydrocarbon : F_2 Ratio	1:73	1:33	1:49	1:73	1:16
Percent F_2 by Last Stage	4.5%	3.3%	4.5%	3.9%	1.7%
Run Time (hour)	3	3	3	3	3
Products Collected (g)	1.05	1.41	1.37	–	0.80
Theoretical Percent Yields of Perfluorinated Products[b]	48%	58%	53%	30%[c] 20%[d]	20%[e] 34%[f]

1) Pivaloyl chloride; F-Pivaloyl Fluoride. 2) Butyryl chloride; F-Butyryl fluoride 3) Isobutyryl chloride; F-Isobutyryl fluoride 4) Cyclopropylcarbonyl chloride; (c) F-Butyryl fluoride, (d) F-Isobutyryl fluoride 5) Chloroacetyl chloride, (e) F-Acetyl Fluoride (f) Chloro-F-acetyl fluoride.

TABLE A-2

Aerosol Fluorination of (1) 1,2-Dichloro-2-methylpropane, (2)
1,1-Dichloropropane, (3) 3,3-Dichloropentane and (4)
1,1-Dichloroneopentane

Run Parameters	1	2	3	4
Hydrocarbon Throughput				
mmole/hour	2.0	3.7	3.7[a]	2.3[a]
He Carrier (mL/min)	33	50	4	25
Temperature (°C)	22	0	28	28
F_2 Flow (mL/min)				
Stage 1	18	10	20	20
Stage 2	18	20	20	20
Stage 3	18	–	20	20
He Diluent (mL/min)				
Stage 1	75	80	80	80
Stage 2	75	80	80	80
Stage 3	75	80	80	80
Reactor Temps (°C)				
Aerosol Generator	40	40	50	50
Module 1	-45	-45	-45	-40
Module 2	-30	-35	-35	-30
Module 3	10	-10	10	10
Main He Carrier (mL/min)	1000	1000	1000	1000
Hydrocarbon : F_2 Ratio	1:60	1:20	1:208	1:64
Percent F_2 by Last Stage	4.2%	2.3%	4.5%	4.5%
Run Time (hour)	2	2	2	1.5
Products Collected (g)	0.731	1.09	0.185	0.85
Theoretical Percent Yields of Perfluorinated Products				
	63%[b]	30%[c]	51%[e]	26%[g]
		30%[d]	34%[f]	24%[h]

[a] mini bubbler used   [b] 1,3-dichloro-F-methylpropane   [c] 1,1-dichloro-F-propane

[d] 1,2-dichloro-F-propane   [e] XL, XLI, XLII, XLIII (See Appendix B for compound

code)   [f] XXIII, XXIV, XXV   [g] 1,1-dichloro-F-neopentane   [h] chloro-F-neopentane

TABLE A-3

Aerosol Fluorination of trans-1,2-Dichlorocyclopentane (1)
and 1,1-Dichlorocyclopentane (2)

Run Parameters	1	2
Hydrocarbon Throughput		
mmole/hour	1.0	1.8[a]
He Carrier (mL/min)	175	45
Temperature (°C)	22	28
F_2 Flow (mL/min)		
Stage 1	20	20
Stage 2	20	40
Stage 3	20	–
He Diluent (mL/min)		
Stage 1	80	80
Stage 2	80	80
Stage 3	80	80
Reactor Temps (°C)		
Aerosol Generator	45	50
Module 1	-40	-40
Module 2	-30	-35
Module 3	10	10
Main He Carrier (mL/min)	1000	1000
Hydrocarbon : F_2 Ratio	1:146	1:81
Percent F_2 by Last Stage	4%	4.5
Run Time (hour)	3	3
Products Collected (g)	0.843	1.0
Theoretical Percent Yields of Perfluorinated Products[b]		
XXVI[b]	6%	
XXVII	24%	20%
XXXIII	10%	10%
XXXIV	10%	9%
XXXV	9%	9%
XXVI	9%	9%

(a) Minibubbler used

(b) See appendix B for compound code.

TABLE A-4

Aerosol Fluorination of 2,2-Dichloropropane and 1,3-Dichloropropane

Run Parameters	2,2-	1,3-
Hydrocarbon Throughput		
syringe pump mL/hour	0.51	0.51
He Carrier (mL/min)	1	4.5
mL delivered(°C)	0.30	1.70
mmole/hour	2.9	2.9
He primary mL/min	500	500
He secondary mL/min	50	50
He tertiarymL/min	–	–
F_2 Flow (mL/min)		
Stage 1	5	–
Stage 2	10	15
Stage 3	15	15
He Diluent (mL/min)		
Stage 1	150	150
Stage 2	150	150
Stage 3	150	150
Reactor Temperatures (°C)		
Aerosol Generator	100	100
Module 1	–30	–30
Module 2	–20	–20
Module 3	20	20
Main He Carrier (mL/min)	600	600
Hydrocarbon : F_2 Ratio	1:23	1:23
Percent F_2 by Last Stage	1.8%	1.8%
Products Collected (g)	0.242	1.71
Theoretical Percent Yields of Perfluorinated Products		
XXXVIII	10%[a]	–
XXXIX	16%[b]	43%[b]

[a] 1,2-dichloro-F-propane

[b] 1,3-dichloro-F-propane

TABLE A-5

Aerosol Fluorination of (1) 1,1,1-Trichloroethane, (2)
Tetrachloroethylene and (3) 1,1,2,2-Tetrachloroethane

Run Parameters	1	2	3
Hydrocarbon Throughput			
mmole/hour	1.9	2.1	4.0
He Carrier (mL/min)	15	30	70
Temperature (°C)	0	22	28
F_2 Flow (mL/min)			
Stage 1	–	10	18
Stage 2	20	–	–
Stage 3	–	–	–
He Diluent (mL/min)			
Stage 1	80	80	80
Stage 2	80	–	80
Stage 3	–	–	80
Reactor Temperatures (°C)			
Aerosol Generator	40	40	50
Module 1	–45	–45	–45
Module 2	–40	–30	–35
Module 3	–10	10	0
Main He Carrier (mL/min)	1000	1000	1000
Hydrocarbon : F_2 Ratio	1:25	1:12	1:11
Percent F_2 by Last Stage	1.7%	0.9%	1.4%
Run Time (hour)	2	2	2
Products Collected (g)	0.333	0.68	1.010
Theoretical Percent Yields of Perfluorinated Products			
	77%[a]	58%[b]	50%[b]

[a]1,2-dichloro-F-propane, [b]1,1,2,2-tetrachloro-F-ethane

TABLE A-6

Aerosol Fluorination of (1) 2,3-Dichloro-1,4-dioxane and (2)
Bis-(2-chloroethyl) Ether

Run Parameters	1	2
Hydrocarbon Throughput[a]		
mmole/hour	1.8	2.6
He Carrier (mL/min)	120	140
Temperature (°C)	75	28
F_2 Flow (mL/min)		
Stage 1	10	10
Stage 2	10	20
Stage 3	20	20
He Diluent (mL/min)		
Stage 1	60	80
Stage 2	60	80
Stage 3	100	80
Reactor Temps (°C)		
Aerosol Generator	60	50
Module 1	-45	-45
Module 2	-30	-30
Module 3	10	0
Main He Carrier (mL/min)	1000	1000
Hydrocarbon : F_2 Ratio	1:81	1:47
Percent F_2 by Last Stage	2.9%	3.5%
Run Time (hour)	2	2
Products Collected (g)	0.679	1.215
Theoretical Percent Yields of Perfluorinated Products		
	21%[b]	
	35%[c]	54%[e]
	20%[d]	

[a]mini bubbler used, [b]2,3-dichloro-F-1,4-dioxane, [c]2-chloro-F-1,4-dioxane,

[d]F-1,4-dioxane, [e]Bis-(2-chloro-F-ethyl) ether.

TABLE A-7

Aerosol Fluorination of (1) Ethyl-3-chlor_opropanoate and (2)
Isopropyl Propanoate

Run Parameters	1	2
Hydrocarbon Throughput		
mmole/hour	1.75	3.8
He Carrier (mL/min)	190	15
Temperature (°C)	22	28
F_2 Flow (mL/min)		
Stage 1	20	20
Stage 2	30	30
Stage 3	–	–
He Diluent (mL/min)		
Stage 1	100	80
Stage 2	100	120
Stage 3	–	–
Reactor Temps (°C)		
Aerosol Generator	50	50
Module 1	–40	–45
Module 2	–30	–40
Module 3	10	10
Main He Carrier (mL/min)	800	1000
Hydrocarbon : F_2 Ratio	1:70	1:31
Percent F_2 by Last Stage	4.0%	4.0%
Run Time (hour)	3	2
Products Collected (g)	–	–
Theoretical Percent Yields of Perfluorinated Products	–	–

TABLE A-8

Aerosol Fluorination of alcohols

Run Parameters	1[a]	2[b]	3[c]
Hydrocarbon Throughput			
mmole/hour	1.7	2.0	3.8
He Carrier (mL/min)	125	30	20
Temperature (°C)	23	28	24
F_2 Flow (mL/min)			
Stage 1	17	20	20
Stage 2	17	20	20
Stage 3	–	–	20
He Diluent (mL/min)			
Stage 1	80	80	80
Stage 2	80	80	80
Stage 3	–	–	80
Reactor Temps (°C)			
Aerosol Generator	50	50	50
Module 1	-45	-45	-45
Module 2	-30	-30	-30
Module 3	-10	10	10
Main He Carrier (mL/min)	1000	1000	1000
Hydrocarbon : F_2 Ratio	1:49	1:49	1:38
Percent F_2 by Last Stage	2.5%	3.2%	4.5%
Run Time (hour)	3	2	1
Products Collected (g)	–	–	–
Theoretical Percent Yields of Perfluorinated Products	–	–	–

[a] iso-amyl alcohol

[b] 2-butanol

[c] tert-butanol

TABLE A-9

Aerosol fluorination of nitropropane

Run Parameters	1
Hydrocarbon Throughput	
mmole/hour	2.5
He Carrier (mL/min)	80
Temperature (°C)	28
F_2 Flow (mL/min)	
Stage 1	20
Stage 2	15
Stage 3	–
He Diluent (mL/min)	
Stage 1	80
Stage 2	80
Stage 3	–
Reactor Temps (°C)	
Aerosol Generator	50
Module 1	-40
Module 2	-30
Module 3	10
Main He Carrier (mL/min)	1000
Hydrocarbon : F_2 Ratio	1:34
Percent F_2 by Last Stage	2.8%
Run Time (hour)	2
Products Collected (g)	–
Theoretical Percent Yields of Perfluorinated Products[a]	–

[a] F-propane and NO_2

TABLE A-10

Aerosol Fluorination of (1) 1,2-dichloroethane, (2) cis-
and (3) trans-1,2-dichloroethylenes

Run Parameters	1	2	3
Hydrocarbon Throughput			
mmole/hour	2.0	1.2^a	1.4^a
He Carrier (mL/min)	45	10	10
Temperature (°C)	-23	22	22
F_2 Flow (mL/min)			
Stage 1	15	10	10
Stage 2	10	10	10
Stage 3	-	-	-
He Diluent (mL/min)			
Stage 1	80	60	60
Stage 2	80	60	60
Stage 3	80	-	-
Reactor Temps (°C)			
Aerosol Generator	30	45	45
Module 1	-45	-45	-45
Module 2	-35	-30	-30
Module 3	-10	10	10
Main He Carrier (mL/min)	1000	1000	1000
Hydrocarbon : F_2 Ratio	1:30	1:40	1:35
Percent F_2 by Last Stage	1.8%	1.7%	1.7%
Run Time (hour)	2	1	1
Products Collected (g)	0.601	-	-
Theoretical Percent Yields of Perfluorinated Products			
1,2-Dichloro-F-ethane	79%	b	b

[a] iso-amyl alcohol [b] yields not determined on limited quantity.

TABLE A-11

Aerosol Fluorination of (1) 2-Heptanone; (2) 2-Butanone and (3) Acetone

Parameters	Reaction		
	1	2	3
Fluorine flows (cc/min)			
Module 1	20	10	10
Module 2	20	10	10
Module 3	40	20	20
Helium diluent (cc/min)			
Module 1	150	150	150
Module 2	150	150	150
Module 3	150	150	150
Reactor temperatures (°C)[a]			
Module 1	−30	−30	−40
Module 3	−20	−20	−30
Module 3	RT	RT	RT
End coil	RT	RT	RT
Main carrier helium (cc/min)	600	600	600
Evaporator/sublimator temp (°C)	175	100	80
Evaporator/sublimator flows (cc/min)			
Primary	500	500	500
Secondary	50	50	50
Tertiary	0	0	0
Hydrocarbon throughput (mmol/hr	3.8	3.9	5.1
Reaction time (hr)	3.2	4.0	4.0
Overall F_2 :hydrocarbon ratio	51:1	25:1	19:1
Product distribution, % collected	55	20	48
Product yield (grams)	0.348	0.311	0.148
Product yield, % theoretical	8[b]	9[c]	4[d]

[a]RT = room temperature. [b]F-2-Heptanone. [c]F-2-Butanone. [d]F-Acetone.

APPENDIX B

Characterization of Compounds

TABLE B-1
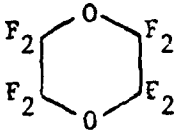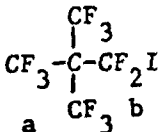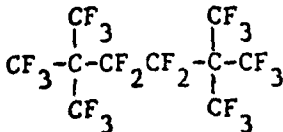
Products in the literature

Number	Compound	NMR (ppm)	IR (cm^{-1})
I	$(CF_3)_3CF$ a b	$\phi_a = -75.3$ [a] $\phi_b = -189.0$	1325, 1300, 1275, [b] 1205, 1170, 995, 730.
II	$(CF_3)_3C{\overset{O}{\underset{F}{\lessgtr}}}$ a b	$\phi_a = -67.1$ [c] $\phi_b = +42.3$	1880, 1855, 1312, [c] 1290, 1215, 990, 739, 710, 660.
III	$HCF_2-\overset{\overset{CF_3}{\mid}}{\underset{\underset{CF_3}{\mid}}{C}}-C{\overset{O}{\underset{F}{\lessgtr}}}$ d a b c	$\phi_a = -127$ [c] $\phi_b = -64$ $\phi_c = +40$ $\delta_d = 6.4$	3000, 1875, 1850, [c] 1400, 1375, 1290, 1260, 1185, 1080, 990, 730, 690.
V	$CF_3CF_2CF_2C{\overset{O}{\underset{F}{\lessgtr}}}$ a b c d	$\phi_a = -82$ [d] $\phi_b = -128$ $\phi_c = -121$ $\phi_d = +31$	1905, 1370, 1280, [b] 1260, 1225, 1205, 1140, 1090, 1070, 960, 760, 690.
VI	$(CF_3)_2CFC{\overset{O}{\underset{F}{\lessgtr}}}$ a b c	$\phi_a = -75.5$ [e] $\phi_b = -182$ $\phi_c = +31$	1887, 1280, 1250, [e] 1319, 1192, 1155, 999.
IX	$(CF_3)_2CHC{\overset{O}{\underset{F}{\lessgtr}}}$ a c b	$\phi_a = -63$ [f] $\phi_b = +38$ $\delta_c = 2.5$	1883, 1300, 1275, [f] 1190, 1150, 1000, 705.
XII	$CF_3C{\overset{O}{\underset{F}{\lessgtr}}}$ a b	$\phi_a = -75.6$ [g] $\phi_b = +15$	1912, 1325, 1235, [b,g] 1200, 1095, 760, 690.
XIII	$CF_2ClC{\overset{O}{\underset{F}{\lessgtr}}}$ a b	$\phi_a = -28$ $\phi_b = +22$	1887, 1364, 1269, [h] 1190, 1105, 976, 966, 863, 767, 690.

TABLE B-1 (Continued)

Number	Compound	NMR (ppm)	IR (cm^{-1})
XV	$CF_3CF_2CF_2Cl$ a b c	$\phi_a = -80.7$[i,j] $\phi_b = -125$	1350, 1300, 1250, [k] 1160, 1145, 1065, 980, 935, 875, 750, 690.
XVIII	$CF_3-CF_2-CF-(CF_3)_2$ a b c d	$\phi_a = -81.2$ [l] $\phi_b = -119.9$ $\phi_c = -187.4$ $\phi_d = -72.9$	1260, 1255, 1225, [m] 1147, 1090, 1060, 980, 930, 888, 720, 635, 610, 525.
XXI	$CF_3CFClCF_3$	$\phi_a = -81.4$ [n] $\phi_b = -144.6$	1302, 1255, 1190, [o] 1136, 972, 763, 720.
XXVI	cy-C_5F_{10}	$\phi_a = -132.9$	1325, 1280, 1220, [b] 1050, 985.
XXVII	$\begin{array}{c} CH_3 \\ | \\ CH_3 - C - CH_2Cl \\ | \\ F \end{array}$ b a c	$\phi_a = -140.5$ [p] $\delta_b = 1.44$ $\delta_c = 3.54$	
XXXI	CF_2ClCF_2Cl a a	$\phi_a = -71.2$ [q]	1275, 1190, 1140, [r] 1040, 930, 850, 680.
XXXVII	$CFCl_2-CF_2-CF_3$ a b c	$\phi_a = -63$ $\phi_b = -121$ $\phi_c = -77$	1325, 1239, 1212, [s] 1115, 907, 838, 739.
XXXVIII	$CF_2Cl-CFCl-CF_3$ a b c	$\phi_a = -63.8$ [t] -64.8 $\phi_b = -133.2$ $\phi_c = -76.4$	1282, 1239, 1131, [s] 1071, 1044, 970, 851, 727.

TABLE B-1 (Continued)

Number	Compound	NMR (ppm)	IR (cm^{-1})
XXXIX	$CF_2Cl-CF_2-CF_2Cl$ a　　b　　a	$\phi_a = -67.9$ [j] $\phi_b = -119.4$	1265, 1205, 1150, [u] 1110, 1020, 995, 910, 870, 845, 770.
XLV	$CF_2Cl-CFCl_2$	$\phi_a = -68.4$ [v,w] $\phi_b = -72.5$	1195, 1155, 1095, [y,x] 1030, 895, 800, 695, 625.
XLVI	$CFCl_2-CFCl_2$ a　　a	$\phi_a = -67.8$ [y,z]	1140, 1110, 1085, [a'] 1025, 930, 900, 880, 835, 780, 750.
XLVII	(cyclic structure with O, F_2 groups)	$\phi_a = -82.0$ [b']	1320, 1250, 1165, 1030, 900, 670.
LXV	$CF_3-\overset{CF_3}{\underset{CF_3}{C}}-CF_2I$ a　　b	$\phi_a = -63.34$ [c'] $\phi_b = -42.73$	1285, 1270, 1220, [c'] 1120, 1025, 988, 809, 751, 730, 720.
LXXII	$CF_3-\overset{CF_3}{\underset{CF_3}{C}}-CF_2CF_2-\overset{CF_3}{\underset{CF_3}{C}}-CF_3$	$\phi_a = -63.4$ [d'] $\phi_b = -99.2$	1295, 1280, 1229, [d'] 1170, 1125, 995, 790, 750, 739, 710.

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TABLE B-2

1,3-Dichloro-F-2-methylpropane (XXXII)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

$$CF_3 \text{ b}$$
$$|$$
$$CF_2Cl-CF-CF_2Cl$$
$$\text{a} \quad \text{c} \quad \text{a}$$

ϕ_a = -60.1 ppm (d.q)

ϕ_b = -71.4 ppm (d.p)
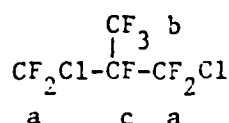
ϕ_c = -167.2 ppm (q.p) J_{ab} = 9.8 Hz

J_{ac} = J_{bc} = 4.9 Hz

MS: m/e (int) ion

CI 255 (1.0) and 253 (23.7) and 251 (36.4) M-F, 237 (34.0) and
235 (100) M-Cl, 149 (2.0) and 147 (6.6) C_3F_4Cl,
87 (15.8) and 85 (48.6) CF_2Cl, 69 (5.6) CF_3.

EI 237 (4.1) and 235 (14.1) M-Cl, 149 (1.8) and 147 (6.1) C_3F_4Cl,

131 (8.6) C_3F_3, 100 (6.7) C_2F_4, 93 (5.8) C_3F_3, 87 (33.1) and
85 (100) CF_2Cl, 81 (1.1) C_2F_3, 69 (48.7) CF_3.

IR: (cm^{-1})

1285(vs), 1255(vs), 1230(vs), 1185(sh), 1170(s), 1150(sh),
1090(s), 1040(s), 930(m), 910(m), 855(s), 830(s) 775(m), 740(m).
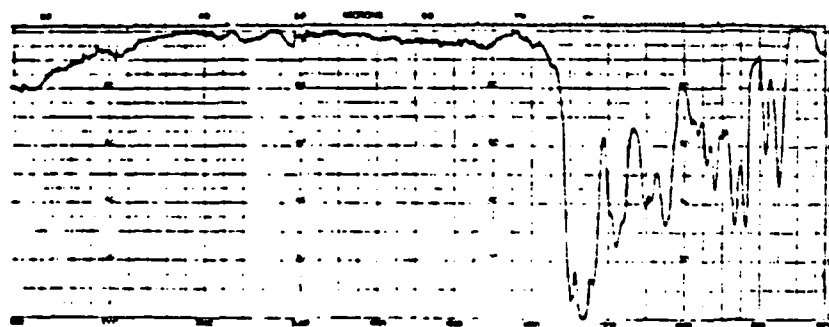
TABLE B-3

NMR assignments of dichloro-F-cyclopentanes

^{19}F NMR: $(\phi_{CFCl_3} = 0$ ppm$)$
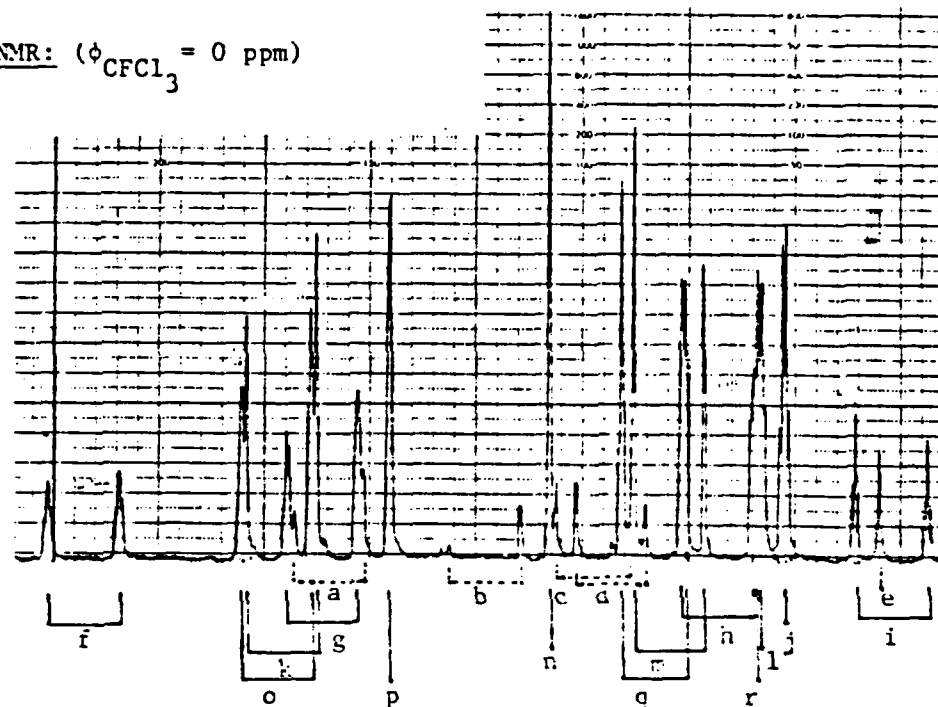
XXXVI

$$\phi_a - \phi_e \quad *$$

XXXV
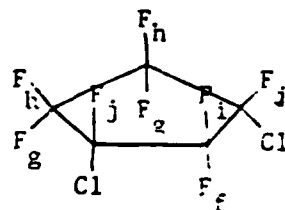
$\phi_f = -104.9$ ppm ⎤
$\phi_i = -138.6$ ppm ⎦ AB $J_{fi} = 257$ Hz

$\phi_g = -114.5$ ppm ⎤
$\phi_n = -131.1$ ppm ⎦ AB $J_{gh} = 255$ Hz

$\phi_j = -134.0$ ppm (q)

* cis-1,2-dichloro-F-pentane: Table B-4 .

TABLE B-3 (Continued)

XXXIII
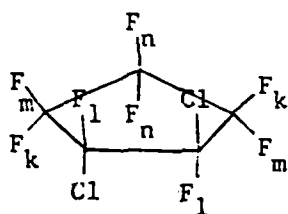
$$\phi_k = -112.8 \text{ ppm} \left.\begin{matrix} \\ \\ \end{matrix}\right\} AB \quad J_{km} = 243 \text{ Hz}$$

$$\phi_m = -129.1 \text{ ppm}$$

$$\phi_1 = -132.9 \text{ ppm (m)}$$

$$\phi_n = -124.0 \text{ ppm (m)}$$

XXXIV

$$\phi_o = -112.6 \text{ ppm} \left.\begin{matrix} \\ \\ \end{matrix}\right\} AB \quad J_{oq} = 245 \text{ Hz}$$
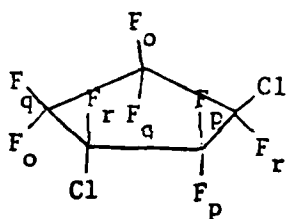
$$\phi_q = -128.4 \text{ ppm}$$

$$\phi_p = -117.4 \text{ ppm (m)}$$

$$\phi_r = -132.7 \text{ ppm (m)}$$

TABLE B-4

Cis-1,2-Dichloro-F-cyclopentane (XXXVI)

$\underline{^{19}F\ NMR:}$ (ϕ_{CFCl_3} = 0 ppm)
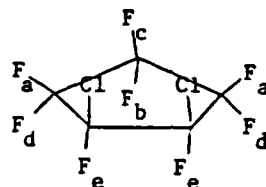
ϕ_e = -137.8 ppm (s)

ϕ_a = -114.8 ppm ⎤
⎬ AB pattern J_{ad} = 241.1 Hz
ϕ_d = -126.3 ppm ⎦

ϕ_b = -121.7 ppm ⎤
⎬ AB pattern J_{bc} = 250.4 Hz
ϕ_c = -125.1 ppm ⎦
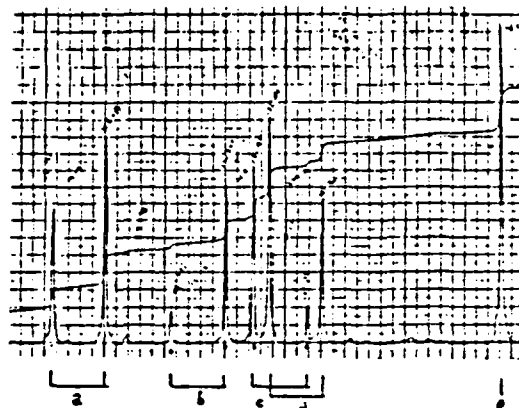
<u>MS:</u> m/e (int) ion

<u>CI</u> 267 (5.4)and 265 (37) and 263 (63) M-F, 249 (4.1) and
247 (14) C_5F_8Cl, 149 (24) and 147 (75) C_3F_4Cl, 93 (11) C_3F_3,
81 (26) C_2F_3, 69 (55) CF_3.

<u>EI</u> 149 (32) and <u>147 (100) C_3F_4Cl</u>, 118 (3.6) and 116 (12) C_2F_3Cl,
69 (14) CF_3.

<u>IR:</u> (cm^{-1})

1330(m), 1300(m), 1240(s), 1210(s), 1100(m), 1040(s), 1000(s),
910(s), 860(s), 820(w).
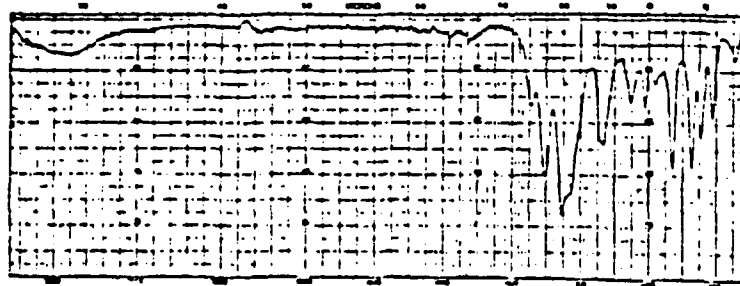
TABLE B-5

Tentative NMR assignments of dichloro-F-pentanes

---

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)　　　　　　　$CF_3CFClCFClCF_2CF_3$　　　　(XLII)
　　　　　　　　　　　　　　　　　　　　　　a　b　c　d　e

ϕ_a = -75 ppm (d.d)

ϕ_b = -131 ppm (m)　　　　　　　　J_{ab} = 6 Hz

ϕ_c = -130 ppm (m)　　　　　　　　J_{ac} = J_{bc} = 12 Hz

ϕ_d = -120 ppm (m)

ϕ_e = -79 ppm (d)

ϕ_a = -77 ppm (t.d)　　　　　　　　$CF_3CFClCF_2CFClCF_3$　　　(XLIII)
　　　　　　　　　　　　　　　　　　　　a　b　c　b　a
ϕ_b = -134 ppm (m)

ϕ_c = -112 ppm (m)　　　　　　　　J_{ab} = 8 Hz　　　J_{ac} = 16 Hz

ϕ_a = -64 ppm (d.m)　　　　　　　　$CF_2ClCF_2CFClCF_2CF_3$　　　(XL)
　　　　　　　　　　　　　　　　　　　　a　b　c　d　e
ϕ_b = -115 ppm (m)

ϕ_c = -135 ppm (m)　　　　　　　　J_{ac} = J_{ce} = 12 Hz

ϕ_d = -124 ppm (m)

ϕ_e = -79 ppm (d)

ϕ_a = -68 ppm (t)　　　　　　　　$CF_2ClCF_2CF_2CFClCF_3$　　　(XLI)
　　　　　　　　　　　　　　　　　　　　a　b　c　d　e
ϕ_b = -119 ppm (m)

ϕ_c = -118 ppm (m)　　　　　　　　J_{ac} = 14 Hz

ϕ_d = -137 ppm (m)　　　　　　　　J_{ce} = 11 Hz

ϕ_e = -81 ppm (t)

TABLE B-6

1,1-Dichloro-F-neopentane (XLIV)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

ϕ_a = -62.99 ppm (d)

ϕ_b = -57.86 ppm (dect)

$$CF_3-\overset{\overset{\displaystyle CF_3}{|}}{\underset{\underset{\displaystyle CF_3}{|}}{C}}-CFCl_2$$

a   b
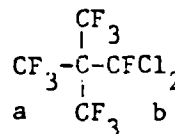
J_{ab} = 12.2 Hz

MS: m/e (int) ion

CI 305 (2.3) and 303 (8.1) and 301 (27.2) M-F, 287 (41) and
285 (100) M-Cl, 69 (43.4) CF_3

EI 199 (12.8) and 197 (31.5) C_4F_6Cl, 181 (45.8) C_4F_7, 103 (5.2) and
101 (14.7) $CFCl_2$, 69 (100) CF_3, 68 (6.6) and 66 (18.2) CFCl.

IR: (cm^{-1})

1300(sh), 1270(vs), 1255(vs), 1220(sh), 1185(m), 990 (m),
840(w), 825(w), 785(w), 750(sh), 730(m), 710(sh).

TABLE B-7

2-Chloro-F-1,4-dioxane (XLVII)

---

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)
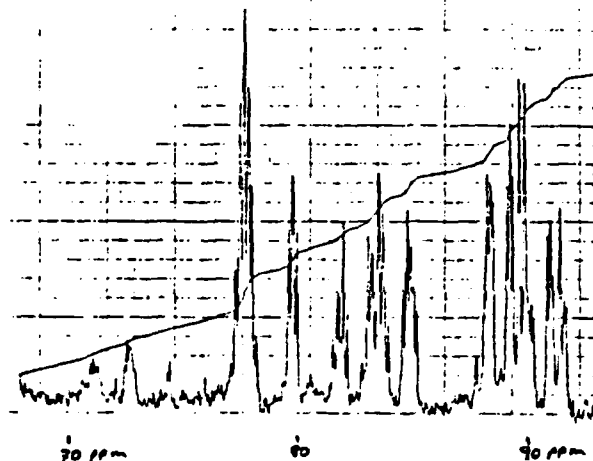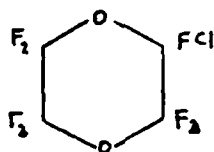
MS: m/e (int) ion

CI 213 (99) M-Cl

EI 231 (2.3) and 229 (6.8) M-F, 213 (9.7) M-Cl, 118 (9.5) and
116 (25.5) C_2F_3Cl, 100 (100) C_2F_4.

IR: (cm^{-1})

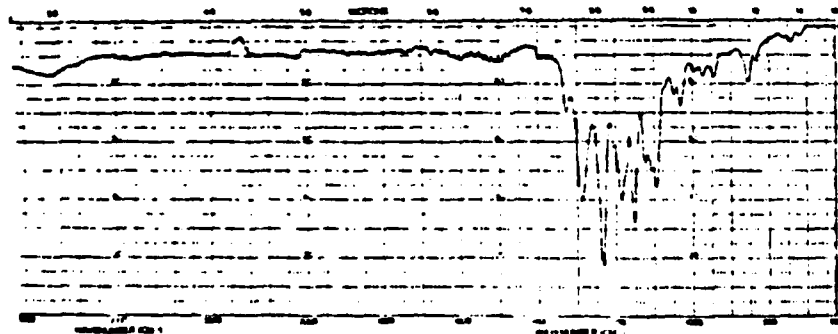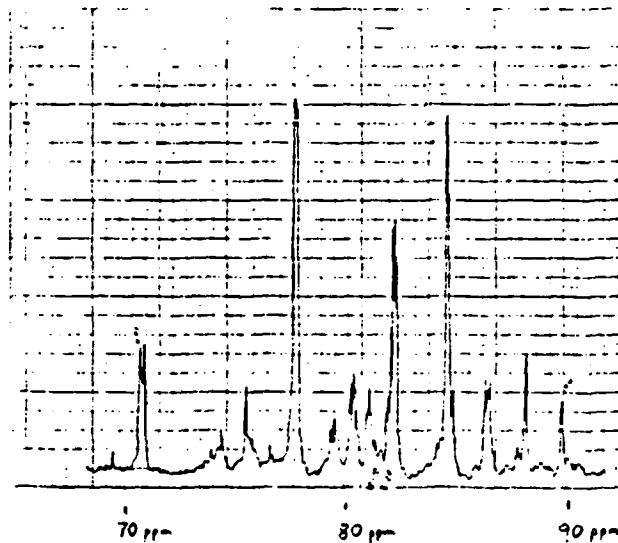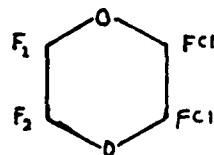1315(w), 1280(m), 1225(s), 1175(m), 1115(m), 1100(m), 1085(m),
1040(w) 1020(w), 845(w).

TABLE B-8

2,3-Dichloro-F-1,4-dioxane (XLVII)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm)

MS: m/e (int) ion

CI 249 (0.6) and 247 (4.0) and 245 (6.2) M-F, 231 (12.1) and
229 (22.3) M-Cl, 194 (100) C$_4$F$_6$O$_2$.

EI 231 (5.1) and 229 (8.5) M-Cl, 194 (32.6) C$_4$F$_6$O$_2$,
100 (100) C$_2$F$_4$.

IR: (cm^{-1})
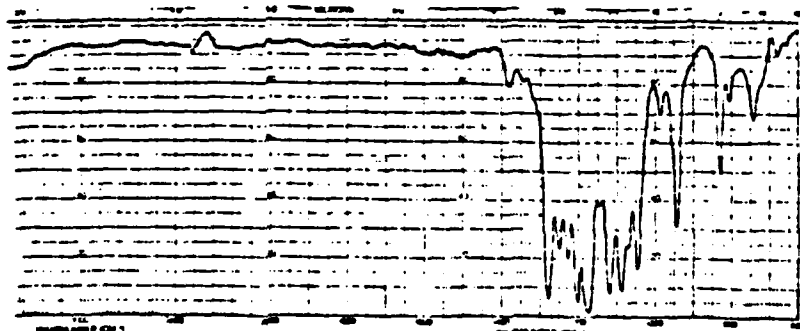
TABLE B-9

F-Bis-(2-chloroethyl)-ether (L)

^{19}F NMR: (ϕ_{CFCl_3} = 0 ppm) $CF_2ClCF_2OCF_2CF_2Cl$
                                              a   b   b   a
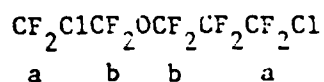
ϕ_a = -74.4 ppm (s)

ϕ_b = -87.7 ppm (s)

MS: m/e (int) ion

CI 272 (0.4) and 270 (3.6) and 268 (4.7) M-F, 153 (0.7) and
    151 (1.2) C_2F_4ClO, 137 (6.3) and 135 (26.5) C_2F_4Cl.
    97 (11.2) C_2F_3O, 87 (31.2) and 85 (100) CF_2Cl.

EI 203 (3.4) and 201 (11.6) M-CF_2Cl, 137 (31.0) and
    135 (100) C_2F_4Cl, 119 43.1) C_2F_5 100 (9.7) C_2F_4,
    87 (13.3) and 85 (42.7) CF_2Cl.

IR: (cm^{-1})

1355(w), 1320(w), 1290(w), 1215(vs), 1185(vs), 1155(vs),
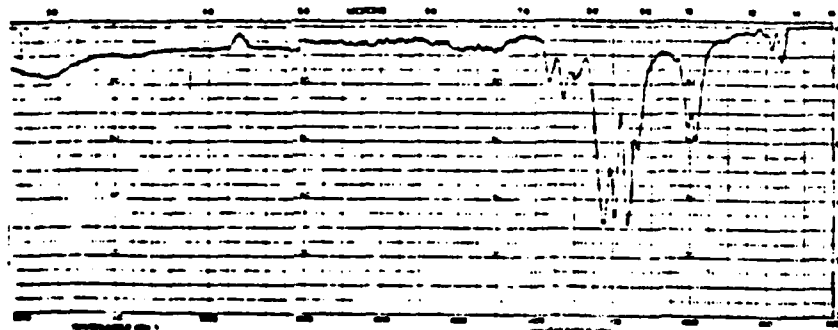1135(m), 995(m), 975(m), 775(w), 750(w).

TABLE B-10

CHARACTERIZATION OF F-2-BUTANONE

Infrared (cm^{-1}):

    1790(m), 1330(w), 1305(m), 1240(vs), 1200(s), 1070(w), 1025(m),

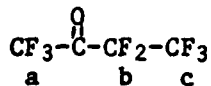   900(m), 875(m), 710(m).

Mass Spectra [m/e(int.)formula]:

  CI(CH_4):

    217(66)C_4F_8OH, M+H; 197(46)C_4F_7O, M-F; 147(14)C_3F_5O; 119(14)C_2F_5;

    97(81)C_2F_3O; 87(21)C_4F_2H; 85(21)CF_3O; 83(5)C_4FO; 71(6)???;

    69(100)CF_3.

  EI(70 eV):

    147(6)C_3F_5O; 119(29)C_2F_5; 100(7)C_2F_4; 97(50)C_2F_3O; 78(3)C_2F_2O;

    70(1)$^{13}CF_3$; 69(100)CF_3; 50(4)CF_2; 32(65)CFH, O_2 (?).

---

^{19}F NMR [ϕ_{CFCl_3} = 0.0 ppm; ϕ(mult.);integral]:

$$CF_3-\overset{\overset{O}{\|}}{C}-CF_2-CF_3$$
$$abc$$

ϕ_a = -75.30 ppm   (t); 3

ϕ_b = -122.11 ppm (q); 2

ϕ_c = -82.28 ppm   (s): 3

J_{ab} = 8.79 Hz

J_{ac}, J_{bc} < 1 Hz

TABLE B-11

CHARACTERIZATION OF F-2-HEPTANONE

Infrared (cm^{-1}):

1790(m), 1360(m), 1300(m), 1245(vs), 1215(s), 1185(s), 1145(s),

1020(m), 975(w), 830(w), 805(m), 740(w), 720(m), 645(m).
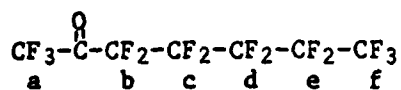

Mass Spectra [m/e(int.)formula]:

CI(CH_4):

366(35)$C_7F_{14}O$, M; 230(4)$C_5F_8OH_2$; 180(2)$C_4F_6OH_2$; 168(2)$C_3F_6OH_2$;

131(7)C_3F_5; 118(6)$C_2F_4OH_2$; 109(1)C_3F_3O; 100(6)C_2F_4; 98(2)C_5F_5,

$^{13}CCF_3O$; 97(74)C_2F_3O; 93(2)C_3F_3; 87(6)C_3FO_2; 78(1)C_2F_2O;

70(1)$^{13}CF_3$; 69(100)CF_3.

EI(70 eV):

269(4)C_5F_{11}; 231(1)C_5F_9; 181(5)C_4F_7; 169(4)C_3F_7; 147(2)C_3F_5O;

131(17)C_3F_5; 119(19)C_2F_5; 109(2)C_3F_3O; 100(8)C_2F_4; 97(48)C_2F_3O;

93(2)C_3F_3; 78(2)C_2F_2O; 70(1)$^{13}CF_3$; 69(100)CF_3.

---

^{19}F NMR [$\emptyset_{CFCl_3}$ = 0.0 ppm; $\emptyset$(mult.);integral]:

$$CF_3-\overset{\overset{O}{\|}}{C}-CF_2-CF_2-CF_2-CF_2-CF_3$$
$$\text{a} \quad \text{b} \quad \text{c} \quad \text{d} \quad \text{e} \quad \text{f}$$

$\emptyset_a$ = -75.17 ppm   (m); 3

$\emptyset_b$ = -118.63 ppm   (m); 2

$\emptyset_{c,d}$ = -122.67 ppm (m); 4   Multiplets are complex.

$\emptyset_e$ = -126.67 ppm   (m); 2

$\emptyset_f$ = -81.30 ppm   (m); 3

APPENDIX C

List of Technical Reports

OFFICE OF NAVAL RESEARCH

Contract No. N00014-77-C-0685

Task No. NR 053-669

List of Technical Reports For the Project Entitled, "LOW TEMPERATURE
FLUORINATION OF AEROSOL SUSPENSIONS OF HYDROCARBONS UTILIZING ELEMENTAL FLUORINE

TR No.	Date Issued	Subtitle (if any)
1	September 1, 1978	
2	April 1, 1980	
3	October 1, 1980	
4	September 1, 1982	
5	February 25, 1983	—— AEROSOL DIRECT FLUORINATION SYNTHESES OF PERFLUOROKETONES
6	April 1, 1983	—— AEROSOL DIRECT FLUORINATION-SYNTHESIS OF PERFLUOROADAMANTANE-THE PENULTIMATE STEP
7	May 31, 1983	—— A SIMPLE PHOTOCHEMICAL CONVERSION OF PERFLUOROALKYL HYDRIDES TO PERFLUORO-ALKYL BROMIDES USING INTERHALOGEN COMPOUNDS
8	July 30, 1983	—— AEROSOL DIRECT FLUORINATION SYNTHESES: ALKYL HALIDES I, NEOPENTYL CHLORIDE AND BROMIDE, FREE RADICALS VERSUS CARBOCATIONS
9	December 30, 1983	—— AEROSOL DIRECT FLUORINATION "INDIRECT SYNTHESES OF PERFLUOROCYCLOKETONES"
10	January 11, 1984	—— AEROSOL DIRECT FLUORINATION: SYNTHESES OF THE HIGHLY BRANCHED KETONES, F-PINACOLONE and "F-PROVALONE"
11	March 15, 1984	—— AEROSOL DIRECT FLUORINATION: ALKYL HALIDES II, CHLORINE SHIFTS AND THE STABILITY OF RADICALS
12	March 30, 1984	—— AEROSOL DIRECT FLUORINATION: SYNTHESES OF THE PERFLUOROALKYL ORTHOCARBONATES, F-TETRAMETHYL AND F-ETHYLENE ORTHOCAR-BONATES

APPENDIX D

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